

Sustainable Heck-Mizoroki and Suzuki-Miyaura Reactions Mediated by Aqueous Palladium Nanoparticles and Imidazolium-Sulfonate Additives

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Electronic Supplementary Information (ESI)

Synthetic Details	p.S3
Figure S1. Appearance of the reaction between ethyl acrylate and iodobenzene in the presence (A) and absence (B) of ImS3b-6.	p.S5
Figure S2. DLS data of the reaction between ethyl acrylate and iodobenzene in the presence of 20 mol% ImS3-b6.	p.S5
Figure S3. Chromatogram and mass fragmentation of 2-octyl-dodecylbromide	p.S6
Figure S4. Chromatogram and mass fragmentation of 2-decyl-tetradecylbromide	p.S6
Figure S5. ¹ H NMR (200MHz) of 3-(1-(2-butyloctyl)-3-imidazolium)propanesulfonate – ImS3b-4 in CDCl ₃	p.S7
Figure S6. ¹ H NMR (200MHz) of 3-(1-(2-hexyldecyl)-3-imidazolium)propanesulfonate – ImS3b-6 in CDCl ₃	p.S8
Figure S7. ¹ H NMR (200MHz) of 3-(1-(2-octyl-dodecyl)-3-imidazolium)propanesulfonate – ImS3b-8 in CDCl ₃	p.S9
Figure S8. ¹ H NMR (200MHz) of 3-(1-(2-decyl-tetradecyl)-3-imidazolium)propanesulfonate – ImS3b-10 in CDCl ₃	p.S10
Figure S9. ¹³ C NMR (100MHz) of 3-(1-(2-butyloctyl)-3-imidazolium)propanesulfonate – ImS3b-4 in CDCl ₃	p.S11
Figure S10. ¹³ C NMR (100MHz) of 3-(1-(2-hexyldecyl)-3-imidazolium)propanesulfonate – ImS3b-6 in CDCl ₃	p.S12
Figure S11. ¹³ C NMR (100MHz) of 3-(1-(2-octyl-dodecyl)-3-imidazolium)propanesulfonate – ImS3b-8 in CDCl ₃	p.S13
Figure S12. ¹³ C NMR (100MHz) of 3-(1-(2-decyl-tetradecyl)-3-imidazolium)propanesulfonate – ImS3b-10 in CDCl ₃	p.S14
Figure S13. ¹ H NMR (200MHz) of methyl cinnamate in CDCl ₃	p.S15
Figure S14. ¹ H NMR (200MHz) of ethyl cinnamate in CDCl ₃	p.S16
Figure S15. ¹ H NMR (200MHz) of <i>tert</i> -butyl cinnamate in CDCl ₃	p.S17
Figure S16. ¹ H NMR (200MHz) of ethyl-3-(4-methoxyphenyl)acrylate in CDCl ₃	p.S18
Figure S17. ¹ H NMR (200MHz) of ethyl-3-(4-acetylphenyl)acrylate in CDCl ₃	p.S19
Figure S18. ¹ H NMR (200MHz) of ethyl-3-(4-nitrophenyl)acrylate in CDCl ₃	p.S20
Figure S19. ¹ H NMR (200MHz) of ethyl-3-(2-methylphenyl)acrylate in CDCl ₃	p.S21

Figure S20. ¹ H NMR (200MHz) of ethyl cinnamate in CDCl ₃ (4-fold reaction scale)	p.S22
Figure S21. ¹³ C (100MHz) NMR of methyl cinnamate in CDCl ₃	p.S23
Figure S22. ¹³ C (100MHz) NMR of ethyl cinnamate in CDCl ₃	p.S24
Figure S23. ¹³ C (100MHz) NMR of <i>tert</i> -butyl cinnamate in CDCl ₃	p.S25
Figure S24. ¹³ C (100MHz) NMR of ethyl-3-(4-methoxyphenyl)acrylate in CDCl ₃	p.S26
Figure S25. ¹³ C (100MHz) NMR of ethyl-3-(4-acetylphenyl)acrylate in CDCl ₃	p.S27
Figure S26. ¹³ C (100MHz) NMR of ethyl-3-(4-nitrophenyl)acrylate in CDCl ₃	p.S28
Figure S27. ¹³ C (100MHz) NMR of ethyl-3-(2-methylphenyl)acrylate in CDCl ₃	p.S29
Figure S28. ¹ H NMR (200MHz) of 4-methoxybiphenyl in CDCl ₃	p.S30
Figure S29. ¹ H NMR (200MHz) of 4-acetylbiphenyl in CDCl ₃	p.S31
Figure S30. ¹ H NMR (200MHz) of 4-hydroxybiphenyl in CDCl ₃	p.S32
Figure S31. ¹ H NMR (200MHz) of 4-aminobiphenyl in CDCl ₃	p.S33
Figure S32. ¹ H NMR (200MHz) of 2-methylbiphenyl in CDCl ₃	p.S34
Figure S33. ¹ H NMR (200MHz) of biphenyl in CDCl ₃ (10-fold reaction scale)	p.S35
Figure S34. ¹³ C (100MHz) NMR of 4-methoxybiphenyl in CDCl ₃	p.S36
Figure S35. ¹³ C (100MHz) NMR of 4-acetylbiphenyl in CDCl ₃	p.S37
Figure S36. ¹³ C (100MHz) NMR of 4-hydroxybiphenyl in CDCl ₃	p.S38
Figure S37. ¹³ C (100MHz) NMR of 4-aminobiphenyl in CDCl ₃	p.S39
Figure S38. ¹³ C (100MHz) NMR of 2-methylbiphenyl in CDCl ₃	p.S40
Figure S39. ¹³ C (100MHz) NMR of biphenyl in CDCl ₃	p.S41
Figure S40. Calibration curves from (a) ethyl cinnamate, (b) iodobenzene and (c) biphenyl	p.S42
Figure S41. Chromatogram and mass fragmentation of ethyl cinnamate and iodobenzene	p.S43
Figure S42. Chromatogram and mass fragmentation of iodobenzene and biphenyl	p.S44
Figure S43. LC/MS-QTOF mass spectra of 3-(1-(2-butyloctyl)-3-imidazolium)propanesulfonate – ImS3b-4	p.S45
Figure S44. LC/MS-QTOF mass spectra of 3-(1-(2-hexyldecyl)-3-imidazolium)propanesulfonate – ImS3b-6	p.S46
Figure S45. LC/MS-QTOF mass spectra of 3-(1-(2-octyl-dodecyl)-3-imidazolium)propanesulfonate – ImS3b-8	p.S47
Figure S46. LC/MS-QTOF mass spectra of 3-(1-(2-decyl-tetradecyl)-3-imidazolium)propanesulfonate – ImS3b-10	p.S48
References	p. S49

SYNTHETIC DETAILS

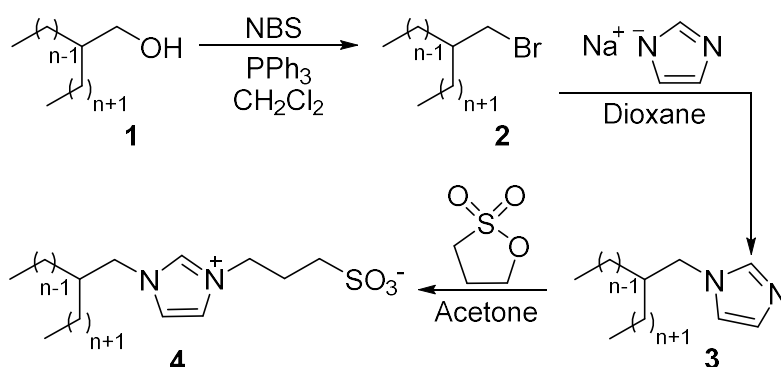
Synthesis of Pd/ImS3-12 nanoparticles

The Pd NPs were synthesized by the methodology previously described by some of us.¹ A mixture containing K₂PdCl₄ (0.15 mmol), NaCl (4.0 mmol) and ImS3-12 (0.50 mmol) in 50 mL of distilled water was magnetically stirred in a 125 mL flask. Then, 5 mL of freshly prepared NaBH₄ solution (12 mg mL⁻¹) was quickly added under vigorous stirring and the yellow solution rapidly turned black, indicating the formation of Pd NPs. The aqueous dispersion was stirred for additional 24 hours and the amount of palladium was determined by FAAS, indicating [Pd] = 2.80 mM. Transmission electron microscopy revealed particles with 3.77±0.58 nm diameter, in agreement the literature.¹

Synthesis of the branched additives ImS3b-n

The additives were prepared as shown in Scheme S1. The first step involved the preparation of the branched alkyl bromides and was adapted from Kastler and coworkers.² In a 125 mL bottom-round flask, a mixture of **1** (22 mmol) and triphenylphosphine (35 mmol) was solubilized in 60 mL of chloroform. *N*-bromosuccinimide (34 mmol) was added in small portions at 0 °C followed by stirring at room temperature for 12 hours. After solvent evaporation, the resulting orange slurry was filtered in a silica bed using hexane as eluent. The hexane solution was concentrated and the **2** was obtained as a colorless oil of high purity as judged by GC-MS (Figure S1 and S2). The second and third steps were performed using the methodologies described by Tondo and coworkers.³ In a 500 mL three-neck round-bottom flask and under argon atmosphere, a solution of imidazole (34.4 mmol) in dioxane (100 mL) was added to a sodium hydride suspension (34.4 mmol) in 150 mL of 1,4-dioxane. The suspension was left for 2 hours at 90 °C. Subsequently, **2** was added drop-wise and the reaction was left for 48 hours at 90 °C. The solvent was evaporated, and the resulting yellow oil was diluted with dichloromethane (100 mL) and washed with water (4x100 mL). Solvent was dried over MgSO₄, filtered and evaporated to furnish **3** as yellowish oil. In the last step, 1,3-propanesultone (11.26 mmol in 30 mL of dry acetone) was added dropwise to a solution of **3** (10 mmol) in 50 mL of dry acetone at 0° C. The reaction was left at room temperature for 5 days, resulting in **4** as a white solid that was filtered, washed with cold acetone (2x10 mL) and left to dry in a desiccator. The global yield for ImS3b-*n* ranged from of 70 to 80% relative to the starting alcohol. All compounds were characterized by ¹H (Figures S5-S8), ¹³C NMR (Figures S9-S12), and LCMS-QTOF (Figures S43-S46).

Scheme S1. Synthesis of the branched ImS3b-*n* additives.



Effect of Pd/ImS3-12 concentration in the Heck-Mizoroki reaction

To a glass ampoule (2 or 5 mL) was added the Pd/ImS3-12 dispersion ([Pd] = 2.80 mM; [ImS3-12] = 9.12 mM), iodobenzene (1.0 mmol; 112 μL), triethylamine (2.0 mmol; 280 μL) and ethyl acrylate (2.0 mmol; 220 μL). The tube was sealed and left in an oil bath at 80 °C with magnetic stirring for 24 hours. After this

period, the products were extracted with ethyl acetate (4x1 mL) and quantification was performed with GC-MS using a calibration curve constructed with an authentic sample of ethyl cinnamate.

Effect of additives in the Heck-Mizoroki reaction

To a 2 mL glass ampoule was added the additive (see table below), water (100 μ L), Pd/ImS3-12 (0.028 mol% Pd, 100 μ L), iodobenzene (1.0 mmol, 112 μ L), triethylamine (2.0 mmol, 280 μ L) and ethyl acrylate (2.0 mmol; 220 μ L). The tube was sealed and left in an oil bath at 80 °C with strong magnetic stirring for 24 hours. Reaction yield was determined as mentioned above.

Table 1. Type and amount of additives used in this work.

Additive	mol%	mass (mg)
ImS3-12	5	17.9
ImS3-12	10	35.8
ImS3-12	20	71.7
1-Propanol	20	12.0
Ethyleneglycol	20	12.4
ImS3b-4	10	35.8
ImS3b-4	20	71.7
ImS3b-6	10	41.5
ImS3b-6	20	82.9
ImS3b-8	10	47.1
ImS3b-8	20	94.2
ImS3b-10	10	52.7
ImS3b-10	20	105.4

Recycling experiments for the Heck-Mizoroki reaction

In a 10 mL round bottom flask was added ImS3b-6 (20 mol%, 331.6 mg), water (400 μ L), Pd/ImS3-12 (0.028 mol% Pd, 400 μ L), triethylamine (8.0 mmol; 1120 μ L) iodobenzene (4.0 mmol; 448 μ L) and ethyl acrylate (8.0 mmol; 880 mL). The reaction was left refluxing in an oil bath at 80 °C with strong magnetic stirring for 24 hours, open to air. After this period, the mixture was extracted with ethyl acetate (4x4 mL). The organic content was diluted in a 25 mL volumetric flask. After that, an aliquot was taken and diluted in a vial to proceed to the GC-MS analysis. The yield was determined using calibration curves of ethyl cinnamate and iodobenzene. The reaction was then repeated by adding the same amount of substrates and base to the initial round bottom flask containing the aqueous dispersion, i.e., no further amount Pd/ImS3-12 and ImS3b-6 were added to the system.

Suzuki-Miyaura reaction

To a 2 mL glass ampoule was added the additive (see table below), water (100 μ L), Pd/ImS3-12 (0.028 mol% Pd, 100 μ L), iodobenzene (1.0 mmol, 112 μ L), triethylamine (2.0 mmol, 280 μ L) and ethyl acrylate (2.0 mmol; 220 μ L). The tube was sealed and left in an oil bath at 80 °C with strong magnetic stirring for 24 hours. Reaction yield was determined as mentioned above.

Figure S1. Appearance of the reaction between ethyl acrylate and iodobenzene in the presence (A) and absence (B) of ImS3b-6 after heating at 80 °C for 1 hour followed by cooling to room temperature (30 minutes).

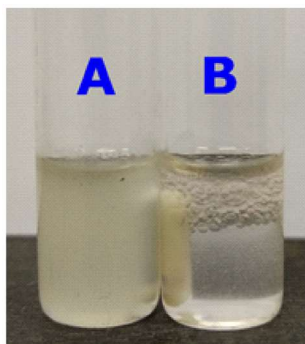
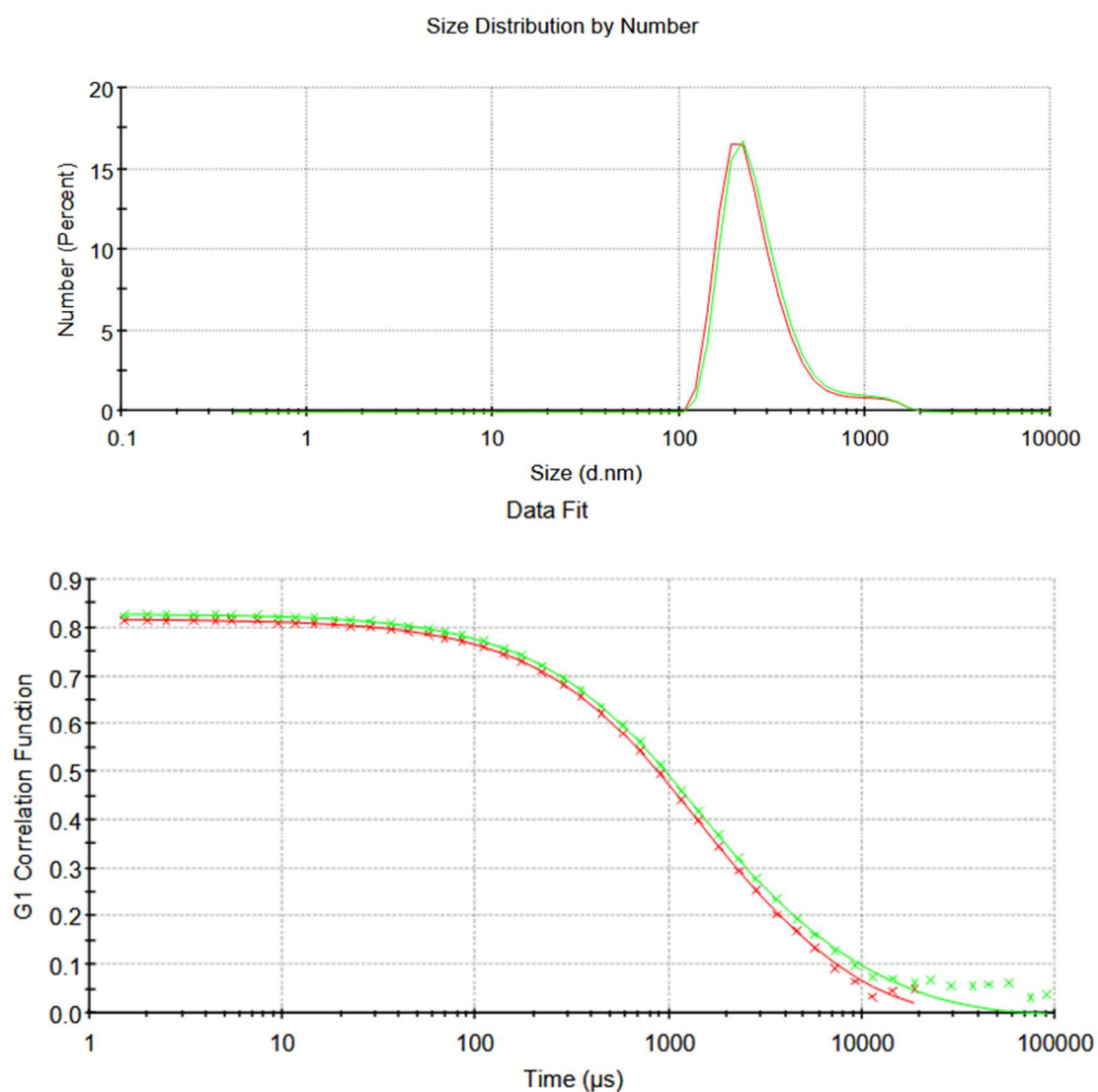


Figure S2. Duplicate DLS data of the reaction between ethyl acrylate and iodobenzene in the presence of 20 mol% ImS3-b6 after 24 h. The reaction contents were diluted 10-fold in water immediately before data acquisition.



GC-MS DATA

Figure S3. Chromatogram and mass fragmentation of 2-octyl-dodecylbromide.

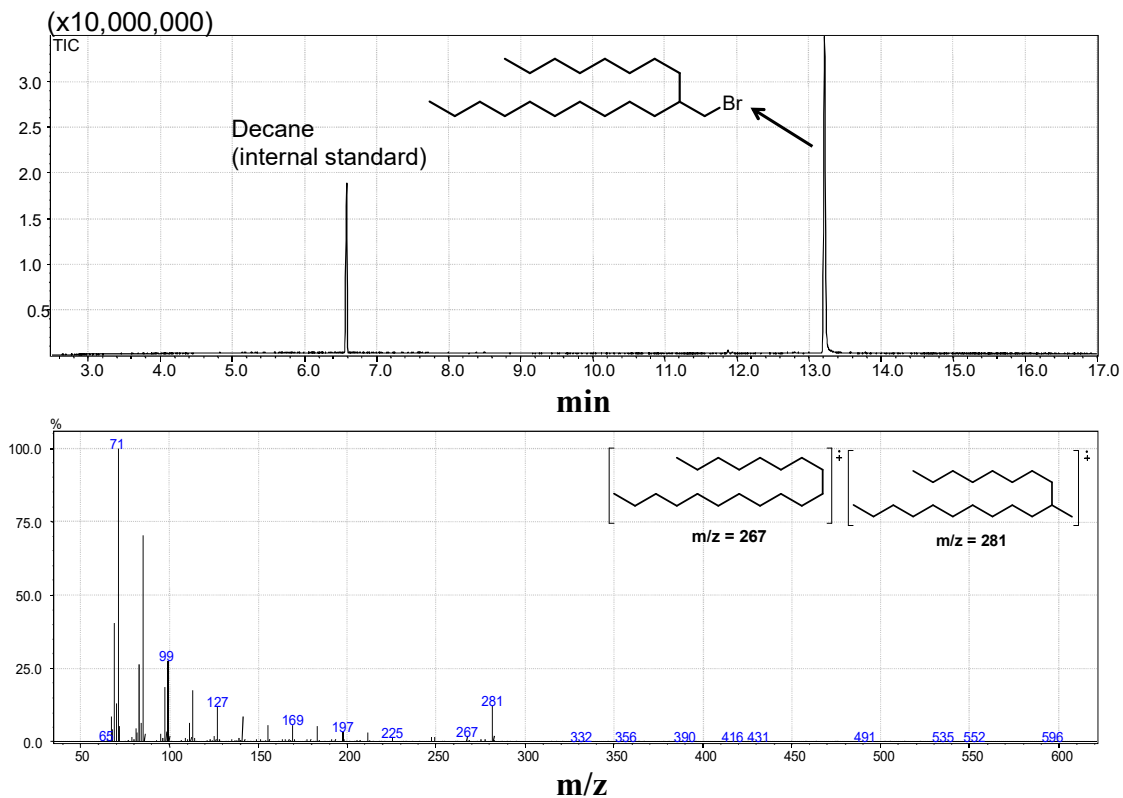
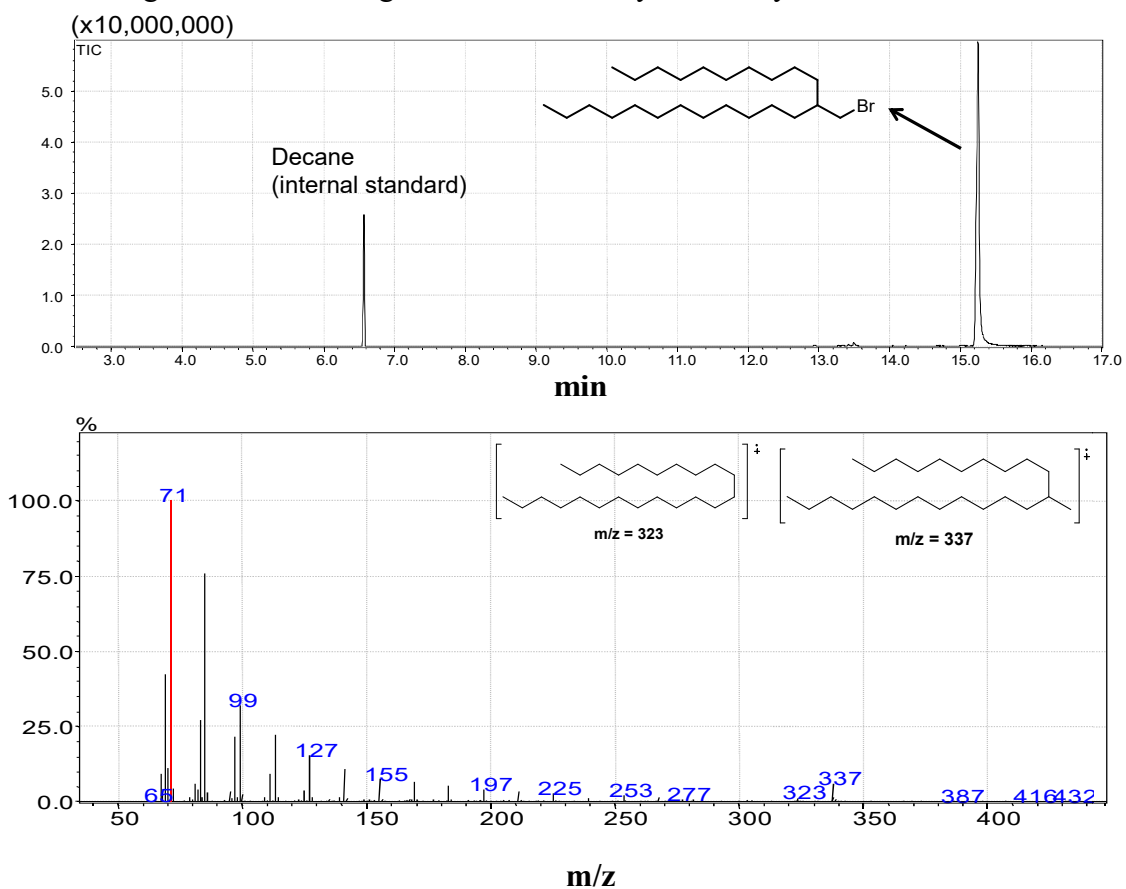


Figure S4. Chromatogram and mass fragmentation of 2-decyl-tetradecylbromide.



^1H NMR and ^{13}C SPECTRA

Figure S5. ^1H NMR (200 MHz) of 3-(1-(2-butylloctyl)-3-imidazolium)propanesulfonate – ImS3b-4 in CDCl_3 using tetramethylsilane (TMS) as internal standard. δ (ppm) 9.55 (s, 1H), 7.67 (s, 1H), 7.16 (s, 1H), 4.59 (t, $J = 7.0$ Hz, 2H), 4.14 (d, $J = 7.1$ Hz, 2H), 2.85 (t, $J = 6.8$ Hz, 2H), 2.38 (d, $J = 7.0$ Hz, 2H), 1.84 (s, 1H), 1.25 (s, 17H), 0.87 (t, $J = 6.3$ Hz, 6H).

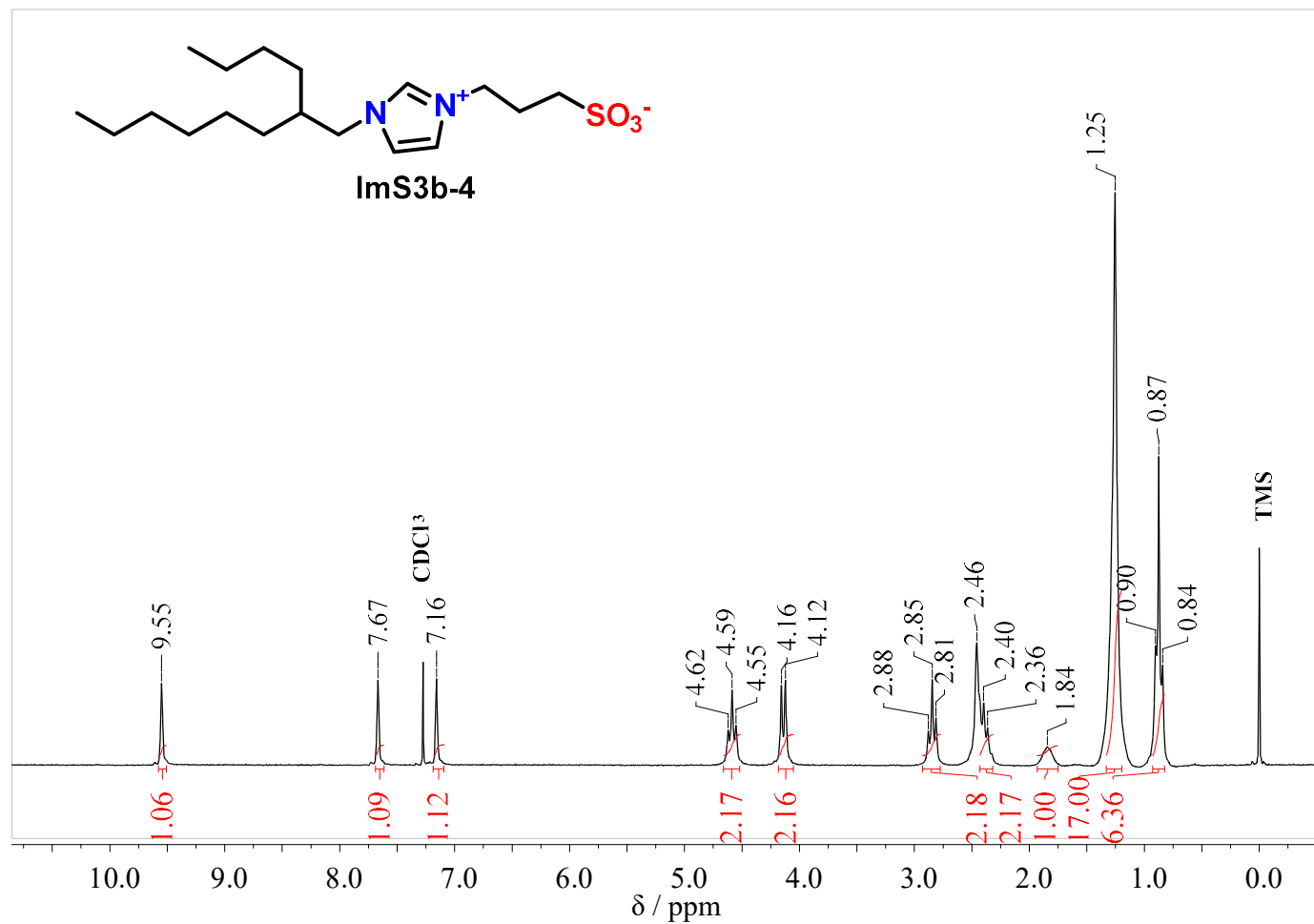


Figure S6. ^1H NMR (200 MHz) of 3-(1-(2-hexyldecyl)-3-imidazolium)propanesulfonate – ImS3b-6 in CDCl_3 using tetramethylsilane (TMS) as internal standard. δ (ppm) 9.62 (s, 1H), 7.63 (s, 1H), 7.13 (s, 1H), 4.60 (t, $J = 6.9$ Hz, 2H), 4.14 (d, $J = 7.0$ Hz, 2H), 2.85 (t, $J = 6.8$ Hz, 2H), 2.46 – 2.37 (m, 2H), 1.85 (s, 1H), 1.25 (s, 24H), 0.88 (t, $J = 6.7, 6.0$ Hz, 6H).

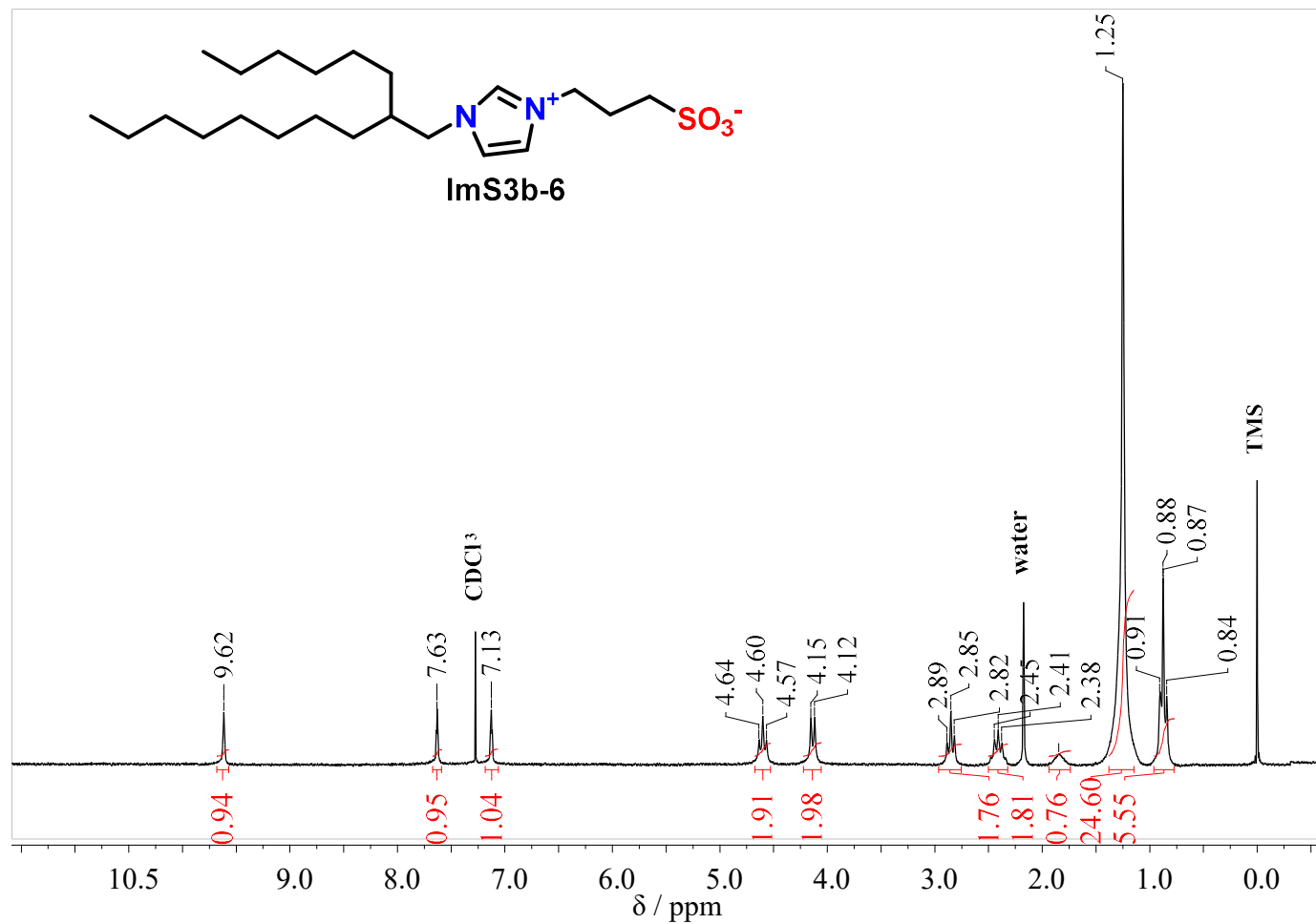


Figure S7. ^1H NMR (200 MHz) of 3-(1-(2-octyldodecyl)-3-imidazolium)propanesulfonate – ImS3b-8 in CDCl_3 using tetramethylsilane (TMS) as internal standard. δ (ppm) 9.58 (s, 1H), 7.61 (s, 1H), 7.12 (s, 1H), 4.60 (t, $J = 6.8$ Hz, 2H), 4.14 (d, $J = 6.9$ Hz, 2H), 2.85 (t, $J = 6.6$ Hz, 2H), 2.52 – 2.28 (m, 2H), 1.78 (s, 1H), 1.25 (s, 32H), 0.88 (t, $J = 6.0$ Hz, 6H).

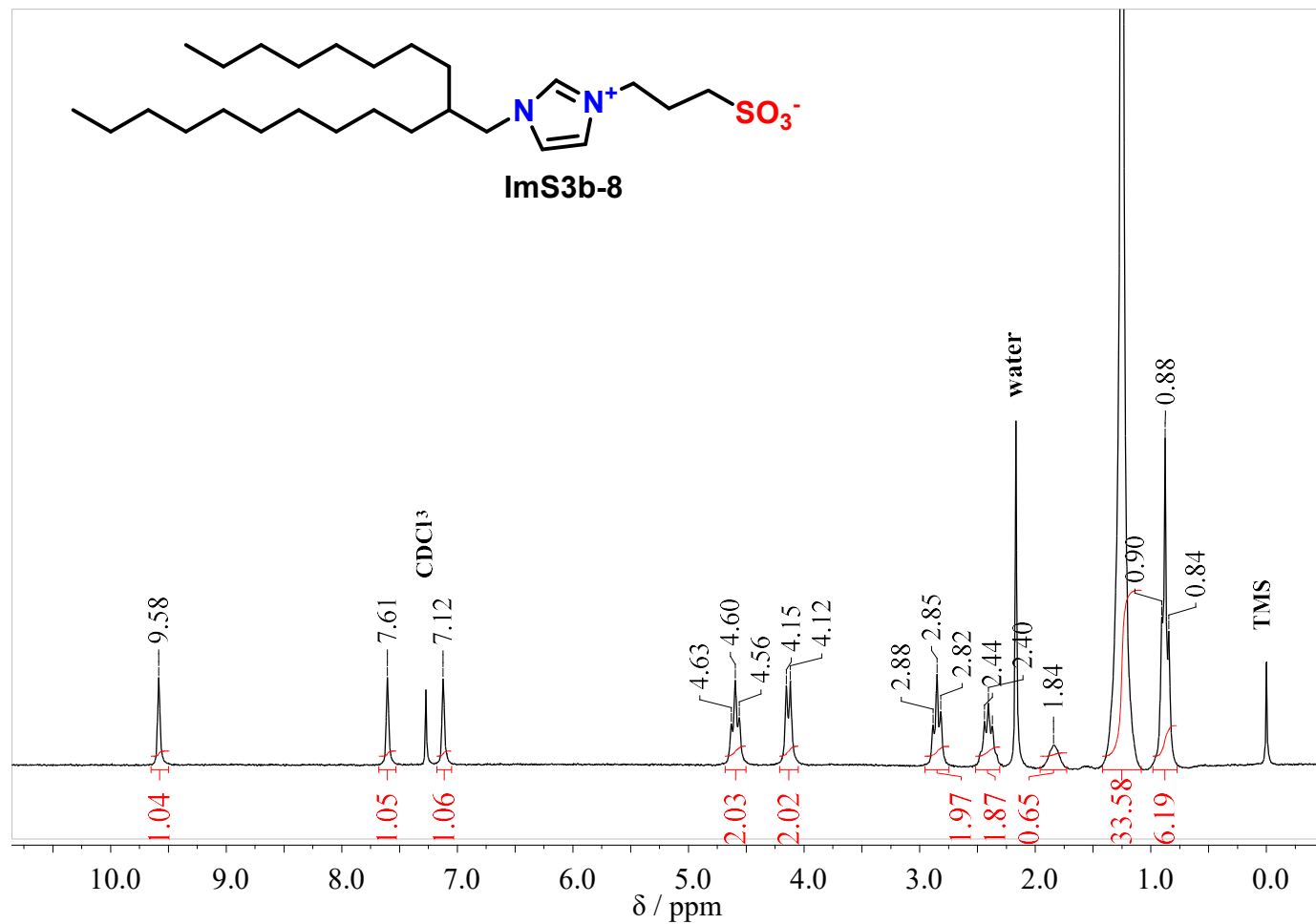


Figure S8. ^1H NMR (200 MHz) of 3-(1-(2-decyltetradecyl)-3-imidazolium)propanesulfonate – ImS3b-10 in CDCl_3 using tetramethylsilane (TMS) as internal standard. δ (ppm) 9.58 (s, 1H), 7.62 (s, 1H), 7.12 (s, 1H), 4.59 (t, $J = 6.4$ Hz, 2H), 4.13 (d, $J = 7.0$ Hz, 2H), 2.85 (t, $J = 6.7$ Hz, 2H), 2.50 – 2.32 (m, 2H), 1.85 (s, 1H), 1.25 (s, 40H), 0.86 (t, $J = 6.6$ Hz, 6H).

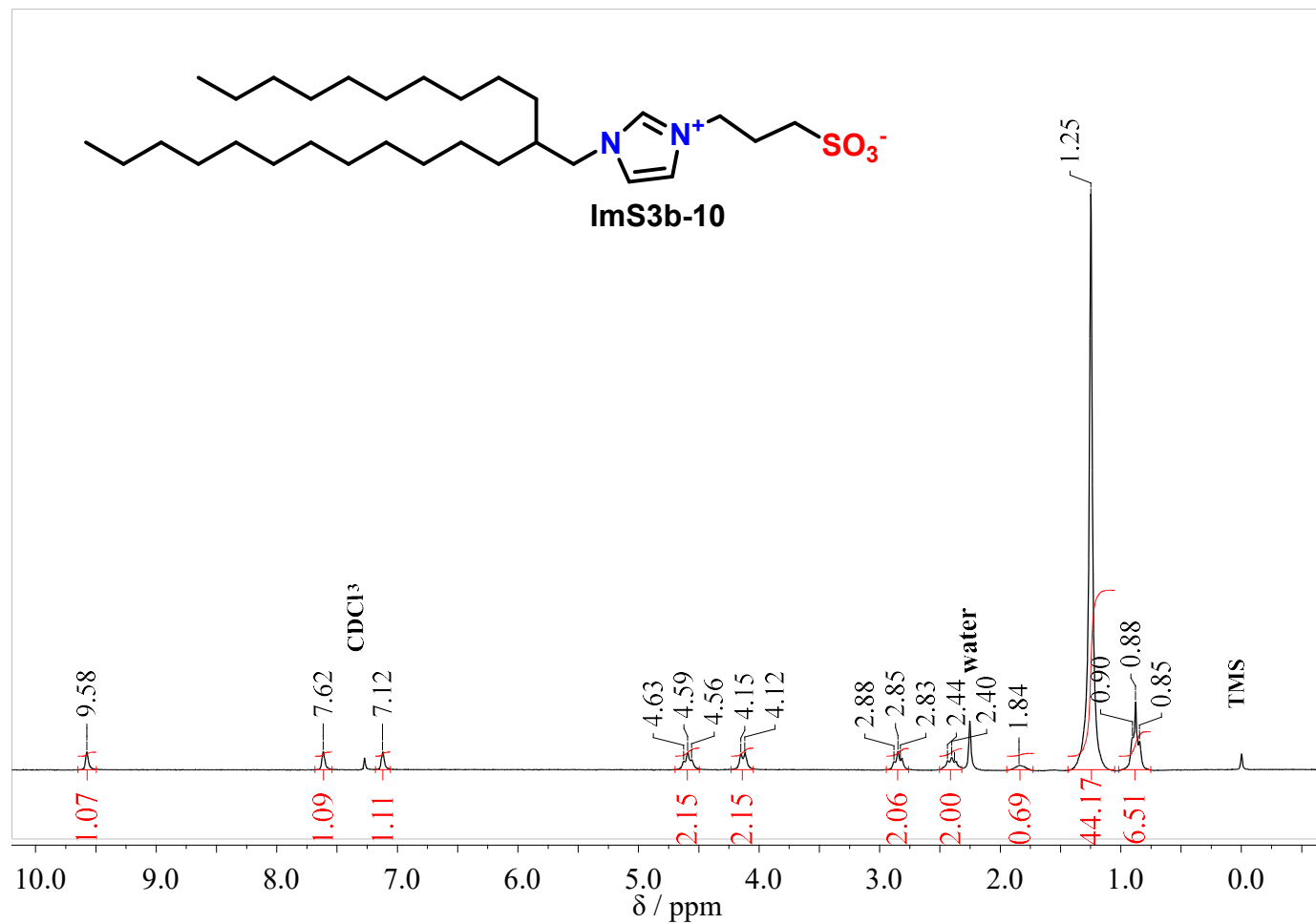


Figure S9. ^{13}C NMR (100 MHz) of 3-(1-(2-butyloctyl)-3-imidazolium)propanesulfonate – ImS3b-4 in CDCl_3 using tetramethylsilane (TMS) as internal standard. δ (ppm) 137.50; 123.13; 121.83; 53.79; 48.51; 47.45; 38.72; 31.67; 29.42; 28.19; 26.65; 26.13; 22.78; 14.04; 13.94.

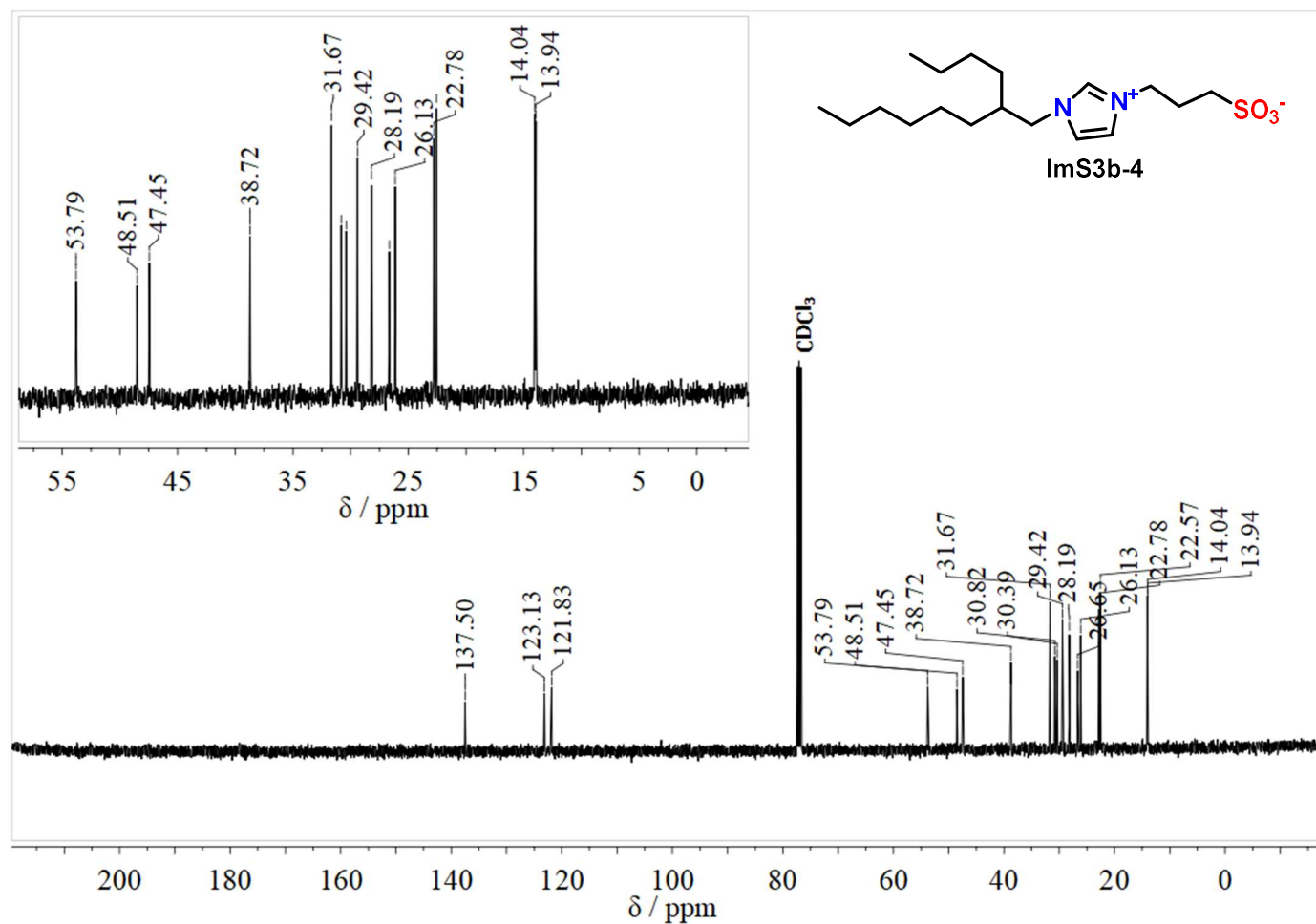


Figure S10. ^{13}C NMR (100 MHz) of 3-(1-(2-hexyldecyl)-3-imidazolium)propanesulfonate – ImS3b-6 in CDCl_3 using tetramethylsilane (TMS) as internal standard. δ (ppm) 137.50; 123.25; 121.72; 53.80; 48.50; 38.72; 31.80; 31.64; 30.75; 29.74; 29.43; 29.39; 29.21; 26.73; 26.13; 26.06; 22.16; 22.54; 14.05; 14.02.

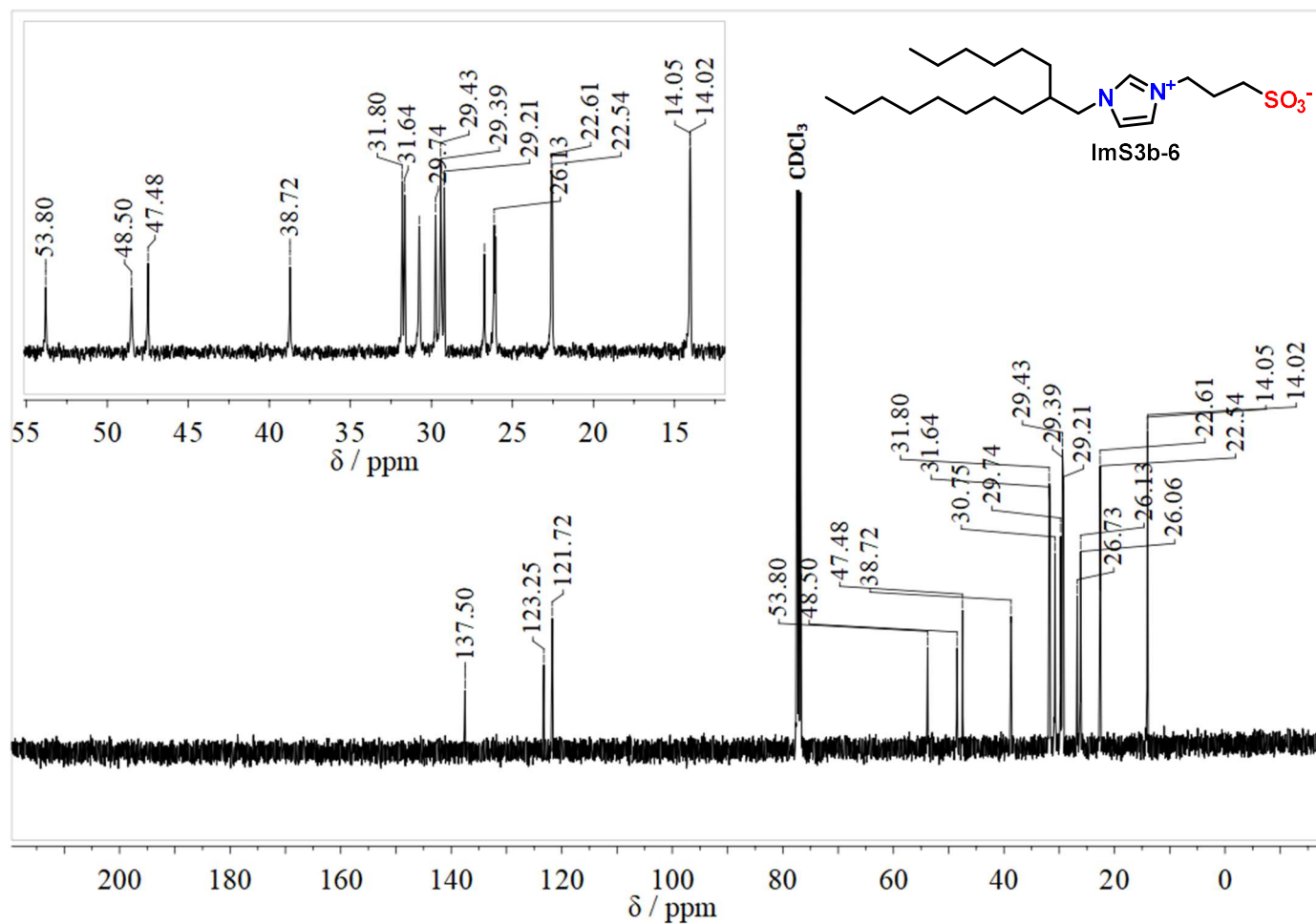


Figure S11. ^{13}C NMR (100 MHz) of 3-(1-(2-octyldodecyl)-3-imidazolium)propanesulfonate – ImS3b-8 in CDCl_3 using tetramethylsilane (TMS) as internal standard. δ (ppm) 137.55; 123.25; 121.66; 53.82; 48.51; 47.48; 38.72; 31.86; 31.81; 30.74; 29.75; 29.57; 29.50; 29.44; 29.29; 29.22; 26.74; 26.13; 22.63; 14.06.

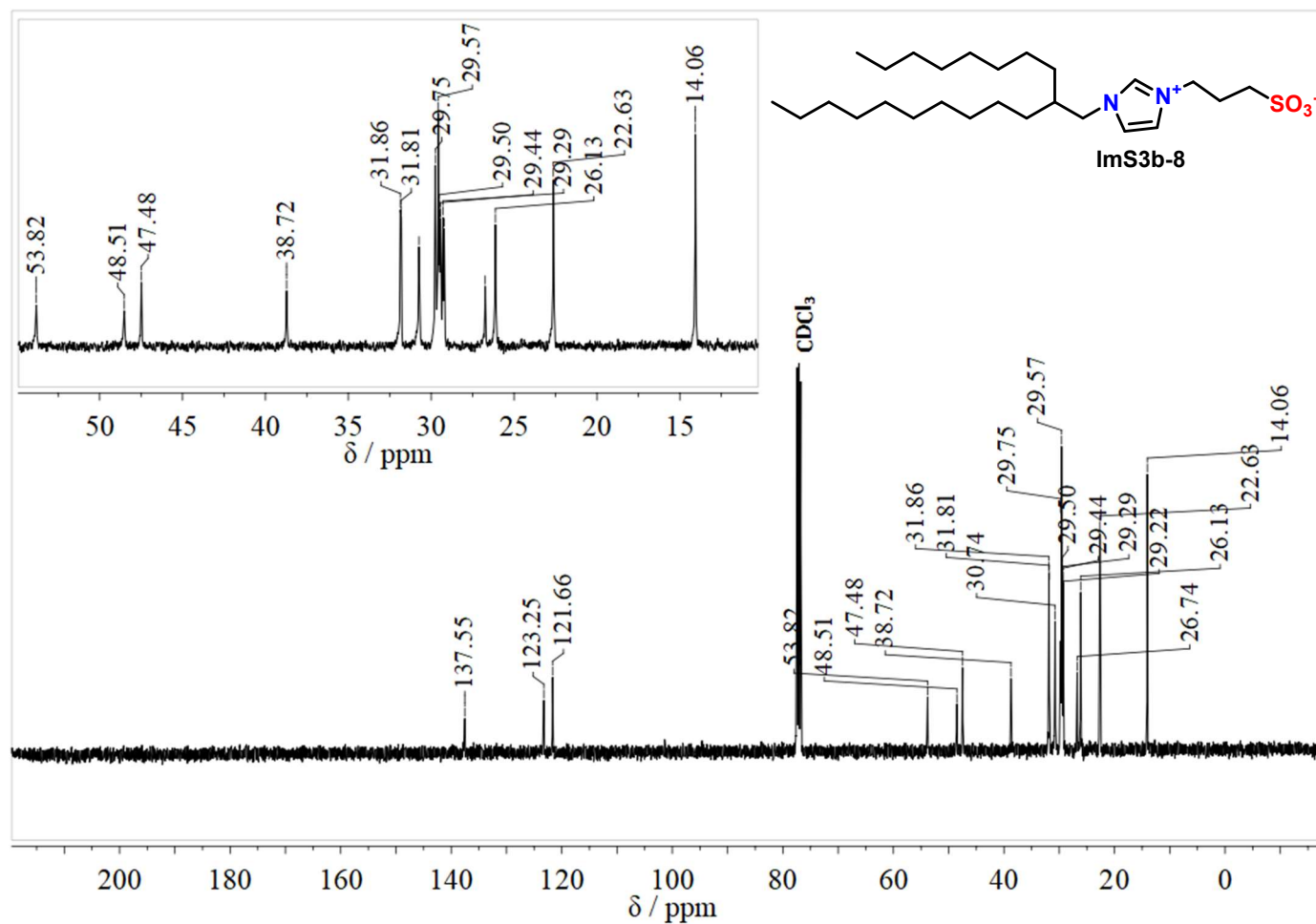


Figure S12. ^{13}C NMR (100 MHz) of 3-(1-(2-decyltetradecyl)-3-imidazolium)propanesulfonate – ImS3b-10 in CDCl_3 using tetramethylsilane (TMS) as internal standard. δ (ppm) 137.60; 123.33; 121.62; 53.80; 48.51; 47.51; 38.71; 31.87; 30.73; 29.76; 29.61; 29.57; 29.50; 29.31; 26.87; 26.13; 22.63; 14.06.

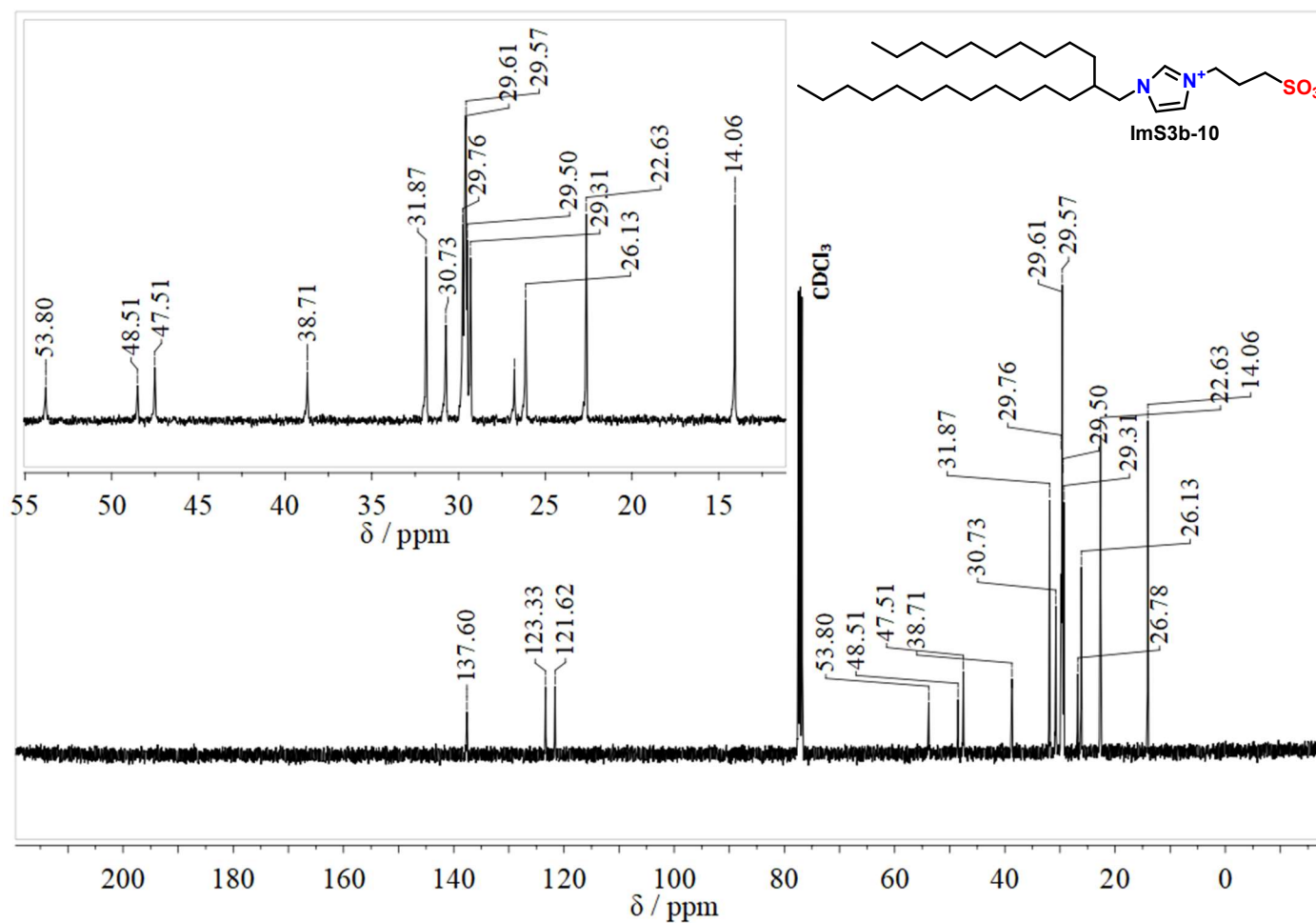


Figure S13. ^1H NMR (200 MHz) of methyl cinnamate in CDCl_3 using tetramethylsilane (TMS) as internal standard. δ (ppm) 7.70 (d, $J = 16.0$ Hz, 1H), 7.53 (dd, $J = 6.5, 3.1$ Hz, 2H), 7.44 – 7.32 (m, 3H), 6.44 (d, $J = 16.0$ Hz, 1H), 3.81 (s, 3H). The peaks at 1.50 and 3.23 ppm are from triethylammonium iodide.

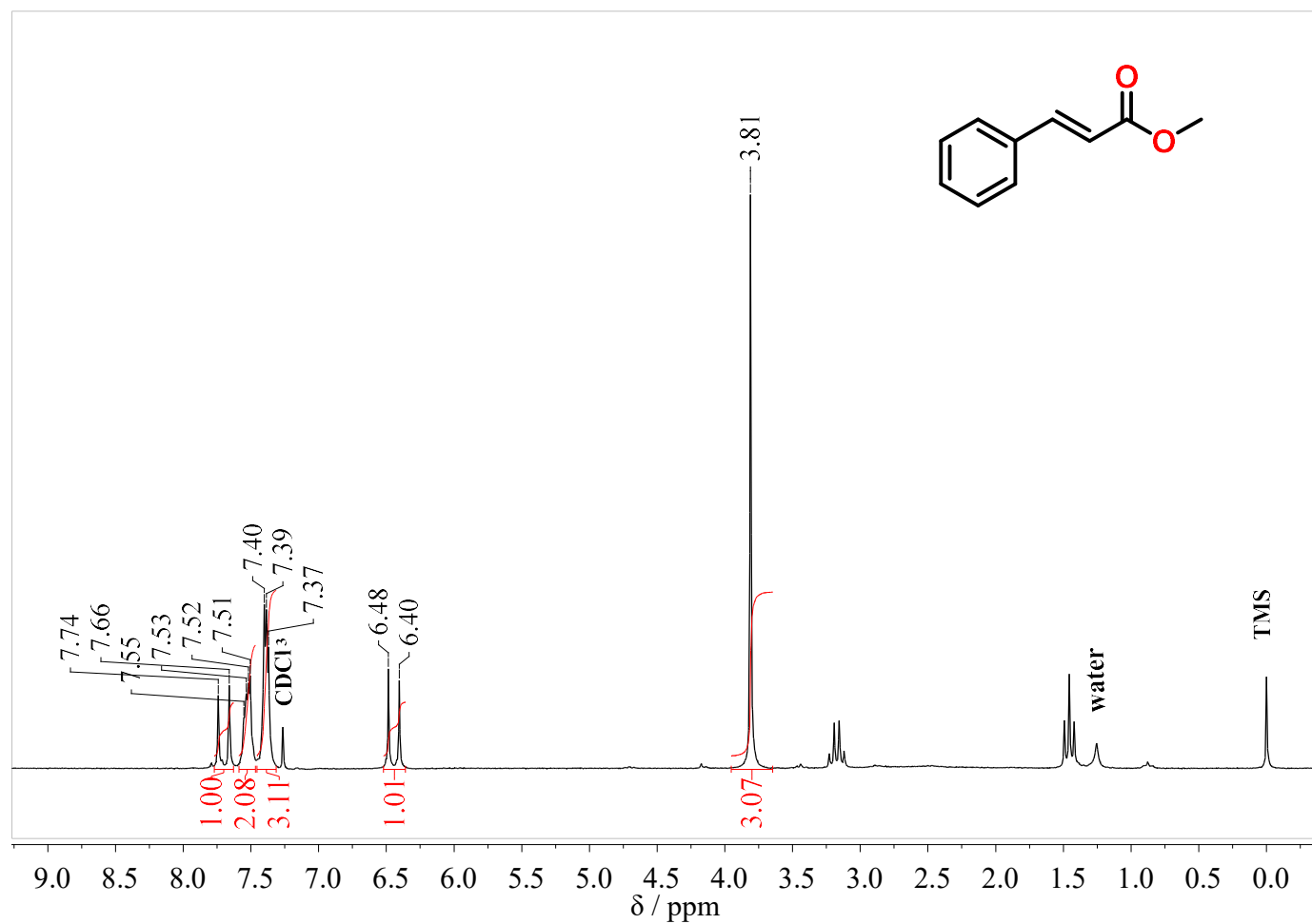


Figure S14. ^1H NMR (200 MHz) of ethyl cinnamate in CDCl_3 using tetramethylsilane (TMS) as internal standard. δ (ppm) 7.69 (d, $J = 16.0$ Hz, 1H), 7.60–7.47 (m, 2H), 7.46–7.31 (m, 3H), 6.44 (d, $J = 16.0$ Hz, 1H), 4.27 (q, $J = 7.1$ Hz, 2H), 1.34 (t, $J = 7.1$ Hz, 3H). The peaks at 1.50 and 3.23 ppm are from triethylammonium iodide.

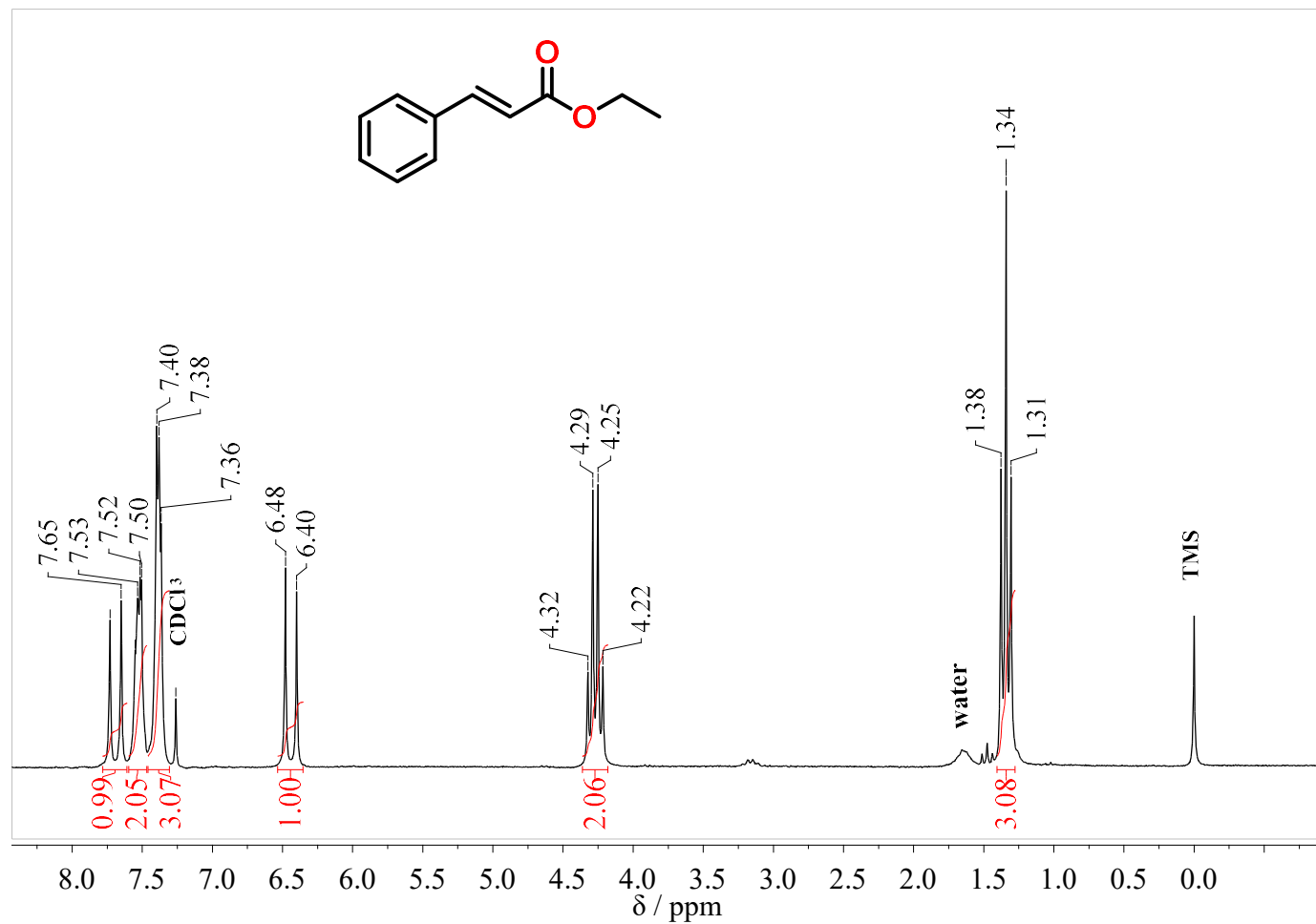


Figure S15. ^1H NMR (200 MHz) of *tert*-butyl cinnamate in CDCl_3 using tetramethylsilane (TMS) as internal standard. δ (ppm) 7.59 (d, $J = 16.1$ Hz, 2H), 7.53–7.43 (m, 4H), 7.43–7.30 (m, 6H), 6.37 (d, $J = 16.0$ Hz, 2H), 1.54 (s, 9H). The peaks at 1.50 and 3.23 ppm are from triethylammonium iodide.

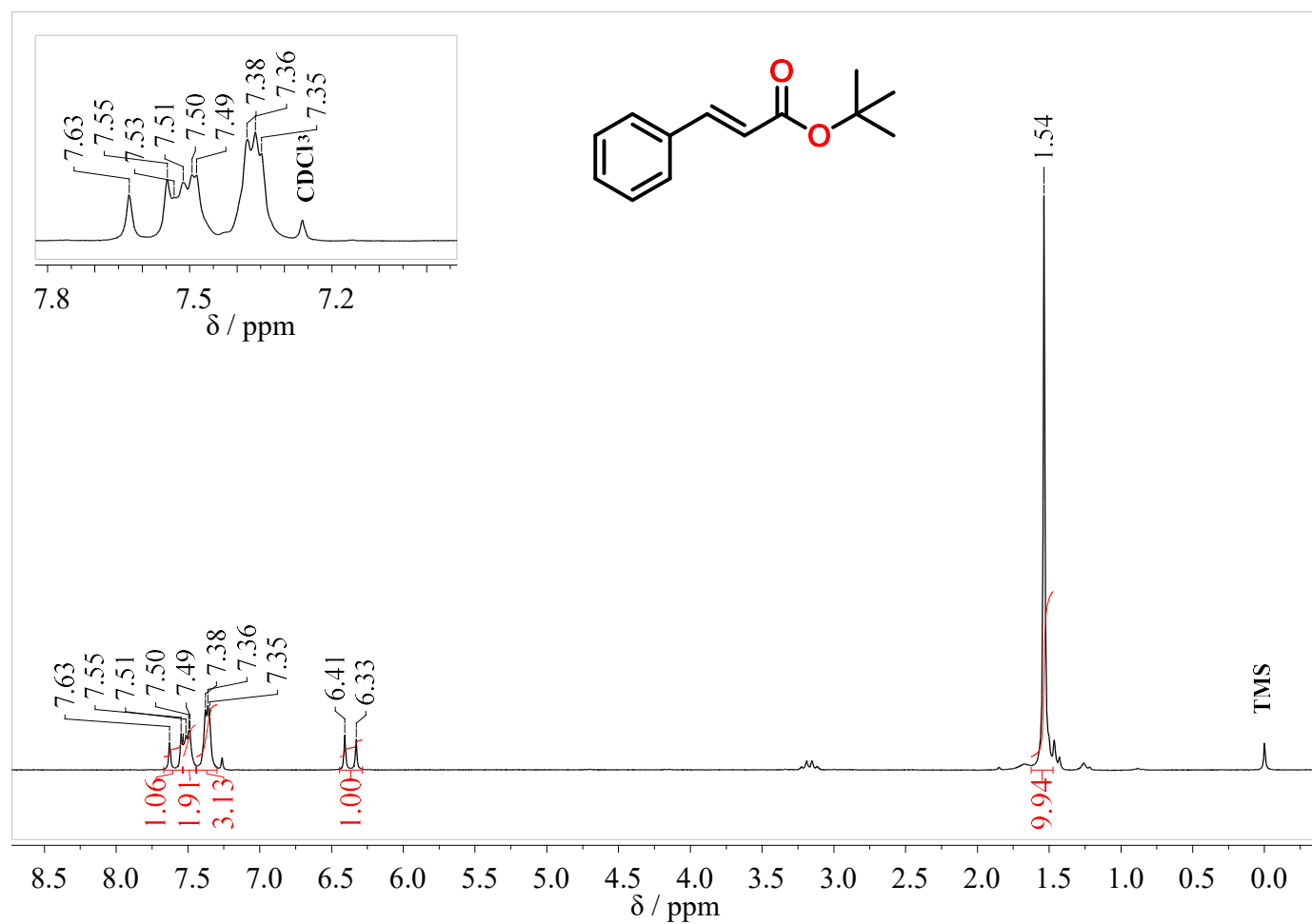


Figure S16. ^1H NMR (200 MHz) of ethyl-3-(4-methoxyphenyl)acrylate in CDCl_3 using tetramethylsilane (TMS) as internal standard. δ (ppm) 7.64 (d, $J = 16.0$ Hz, 1H), 7.48 (d, $J = 8.7$ Hz, 2H), 6.90 (d, $J = 8.7$ Hz, 2H), 6.31 (d, $J = 16.0$ Hz, 1H), 4.25 (q, $J = 7.1$ Hz, 2H), 3.84 (s, 3H), 1.33 (t, $J = 7.1$ Hz, 3H). The peaks at 1.50 and 3.23 ppm are from triethylammonium iodide. The peaks at 3.76, 6.67 and 7.54 ppm are from 4-iodoanisole.

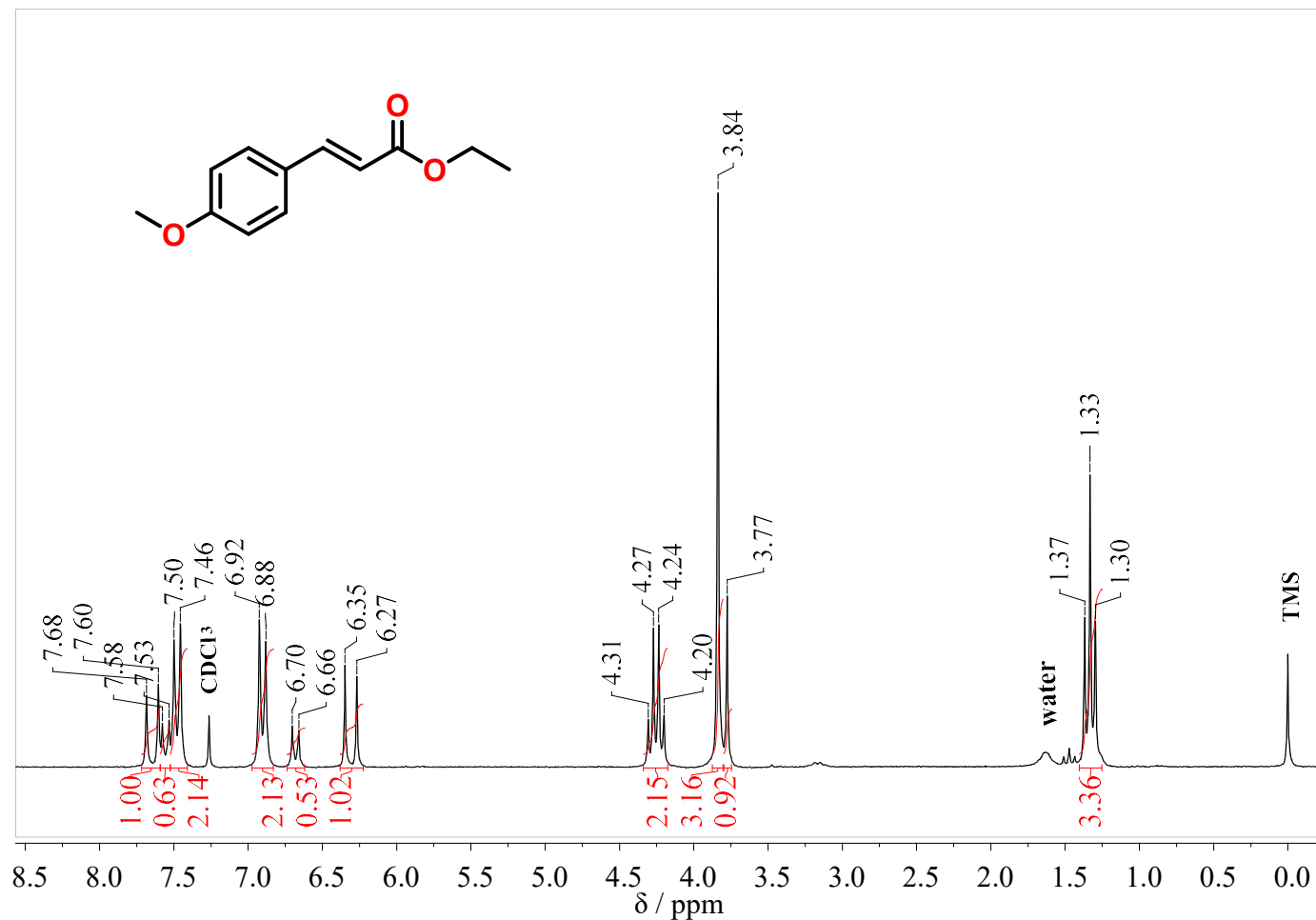


Figure S17. ^1H NMR (200 MHz) of ethyl-3-(4-acetylphenyl)acrylate in CDCl_3 using tetramethylsilane (TMS) as internal standard. δ (ppm) 7.97 (d, $J = 8.7$ Hz, 2H), 7.70 (d, $J = 16.1$ Hz, 1H), 7.61 (d, $J = 8.7$ Hz, 2H), 6.56 (d, $J = 16.1$ Hz, 1H), 4.30 (q, $J = 7.1$ Hz, 2H), 2.62 (s, 3H), 1.35 (t, $J = 7.1$ Hz, 3H).

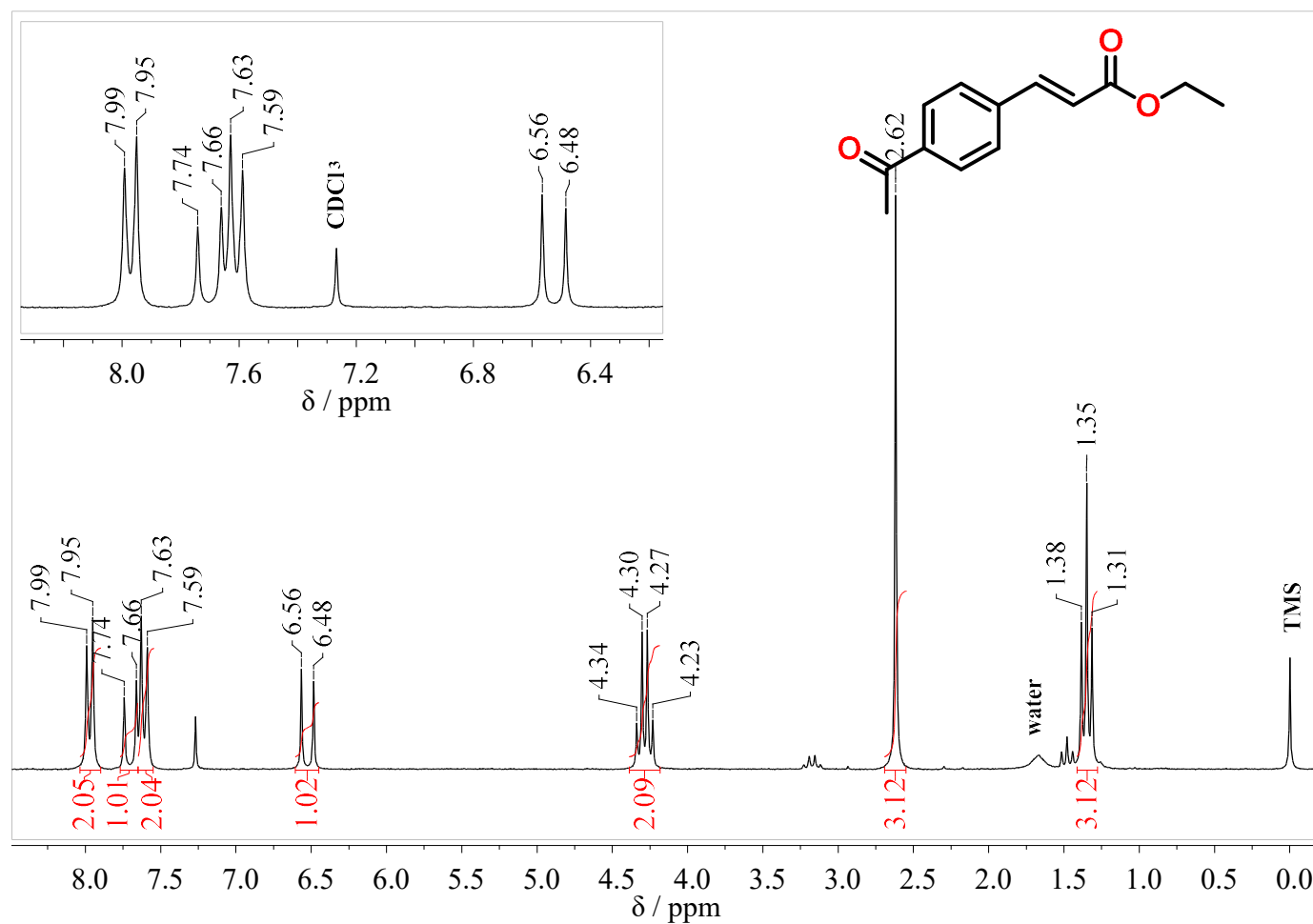


Figure S18. ^1H NMR (200 MHz) of ethyl-3-(4-nitrophenyl)acrylate in CDCl_3 using tetramethylsilane (TMS) as internal standard. δ (ppm) 8.25 (d, $J = 8.7$ Hz, 2H), 7.71 (d, $J = 16.1$ Hz, 1H), 7.67 (d, $J = 8.7$ Hz, 2H), 6.56 (d, $J = 16.1$ Hz, 1H), 4.30 (q, $J = 7.1$ Hz, 2H), 1.36 (t, $J = 7.1$ Hz, 3H).

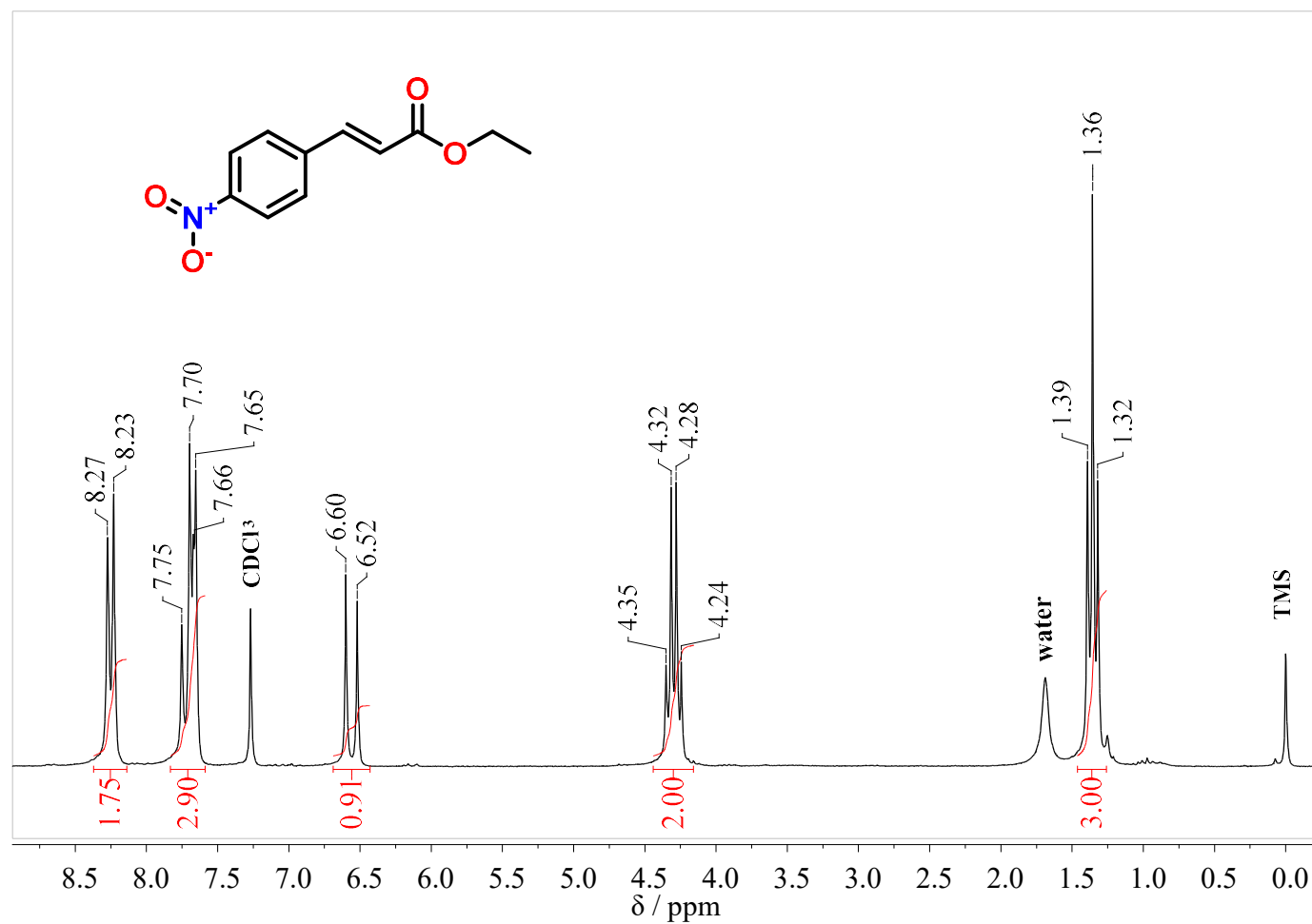


Figure S19. ^1H NMR (200 MHz) of ethyl-3-(2-methylphenyl)acrylate in CDCl_3 using tetramethylsilane (TMS) as internal standard. δ (ppm) 7.97 (d, $J = 15.9$ Hz, 1H), 7.54 (d, $J = 7.0$ Hz, 1H), 7.22 (d, $J = 5.3$ Hz, 3H), 6.36 (d, $J = 15.9$ Hz, 1H), 4.27 (dd, $J = 14.2, 7.1$ Hz, 2H), 2.44 (s, 3H), 1.34 (t, $J = 7.1$ Hz, 3H).

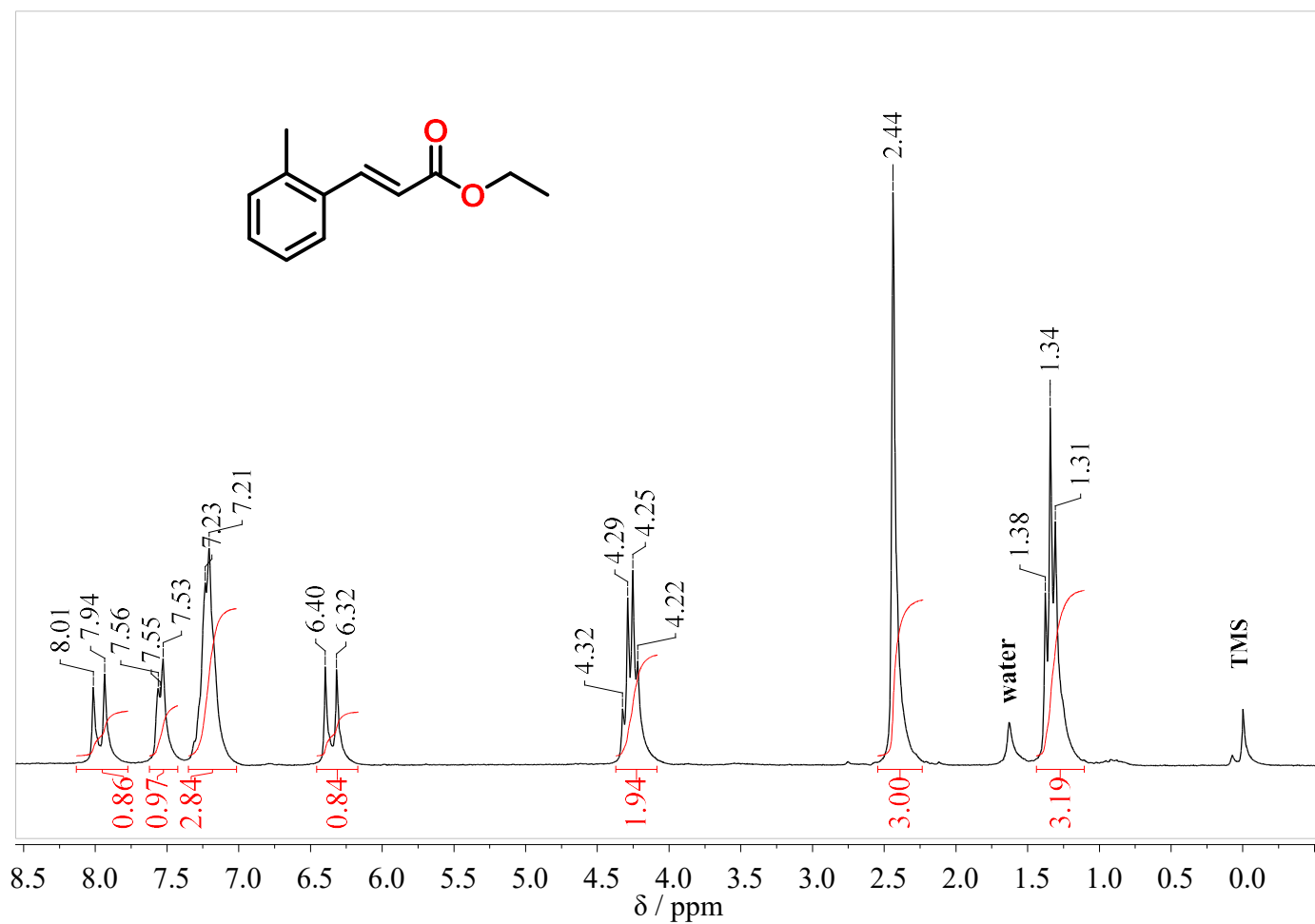


Figure S20. ^1H NMR of ethyl cinnamate in CDCl_3 (4-fold reaction scale) using tetramethylsilane (TMS) as internal standard. δ (ppm) 7.69 (d, $J = 16.0$ Hz, 1H), 7.60 – 7.47 (m, 2H), 7.46 – 7.31 (m, 3H), 6.44 (d, $J = 16.0$ Hz, 1H), 4.27 (q, $J = 7.1$ Hz, 2H), 1.34 (t, $J = 7.1$ Hz, 3H).

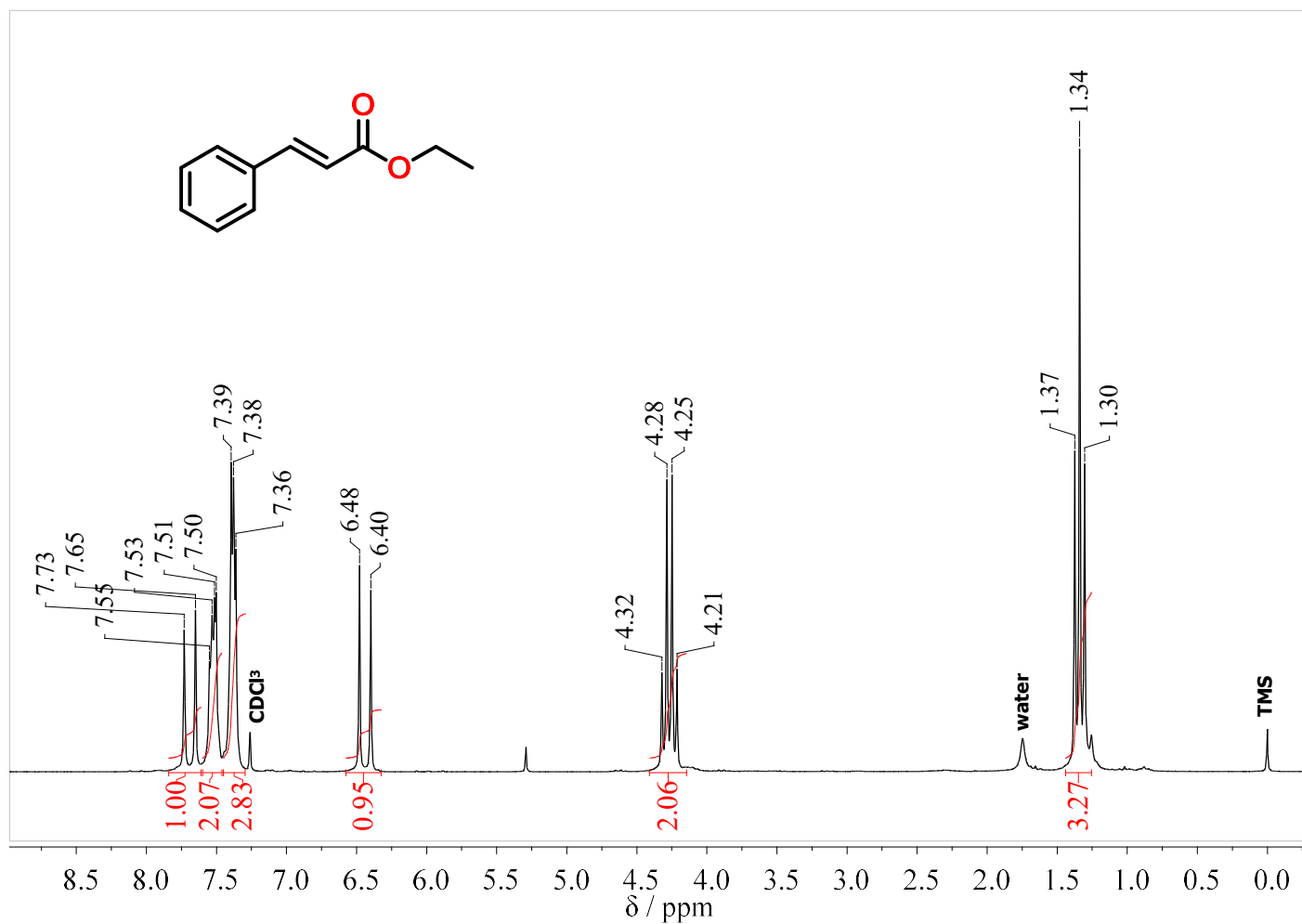


Figure S21. ^{13}C NMR (100 MHz) of methyl cinnamate in CDCl_3 using tetramethylsilane (TMS) as internal standard. δ (ppm) 167.42; 144.88; 134.40; 130.30; 128.89; 128.07; 117.82; 51.60.

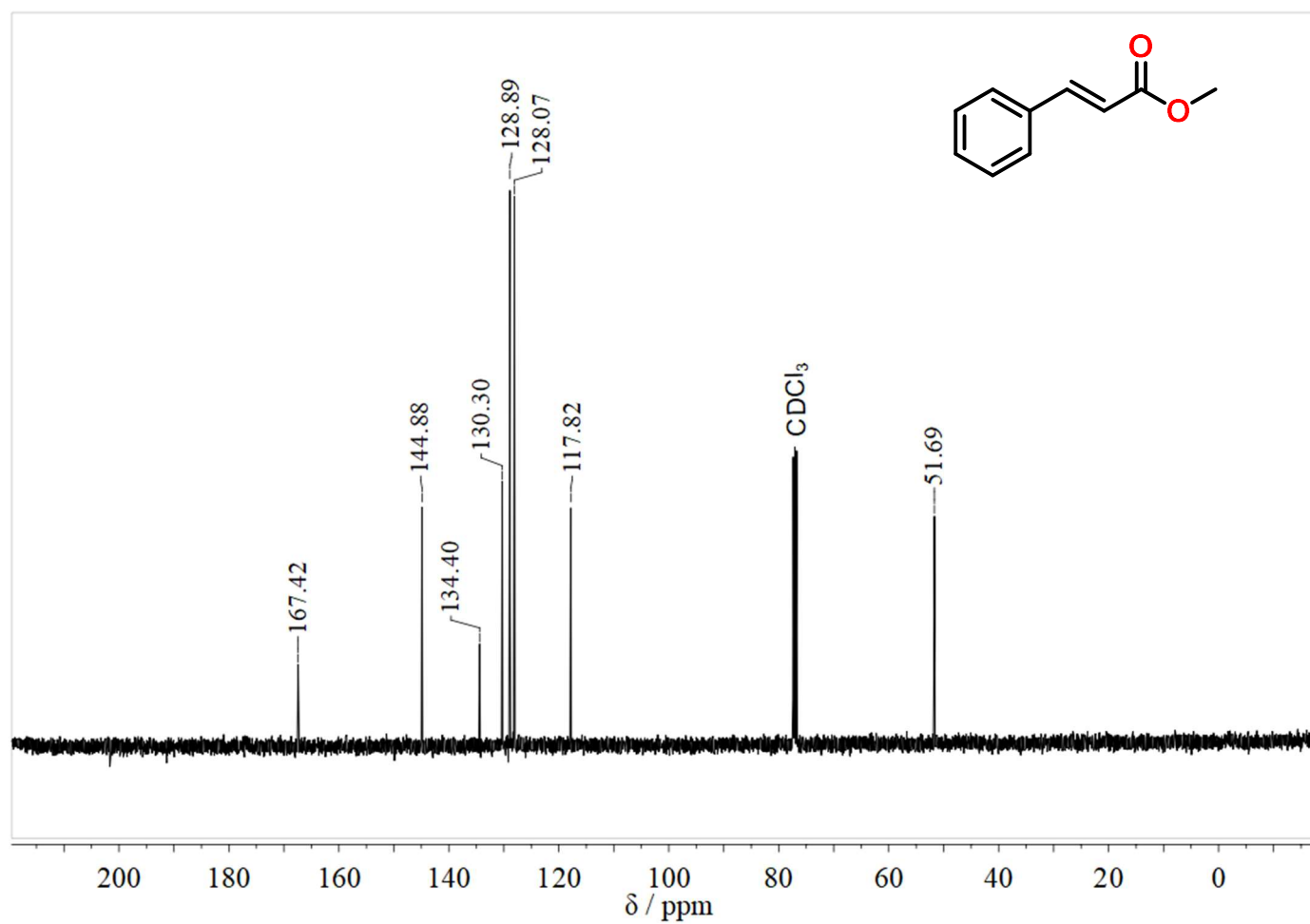


Figure S22. ^{13}C NMR (100 MHz) of ethyl cinnamate in CDCl_3 using tetramethylsilane (TMS) as internal standard. δ (ppm) 167.07; 144.64; 134.47; 130.23; 128.88; 128.06; 118.27; 60.54; 14.32.

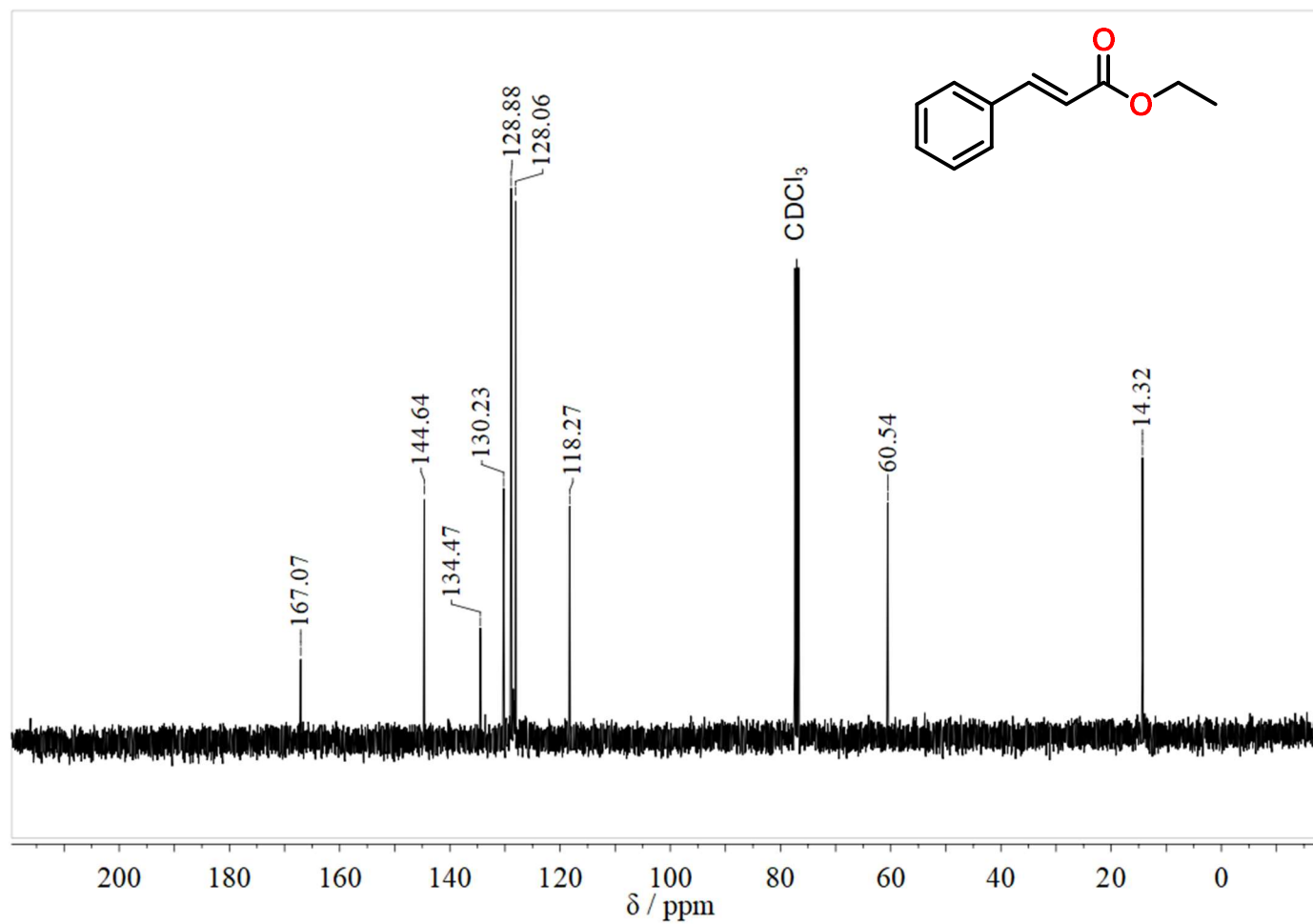


Figure S23. ^{13}C NMR (100 MHz) of *tert*-butyl cinnamate in CDCl_3 using tetramethylsilane (TMS) as internal standard. δ (ppm) 166.33; 143.54; 134.69; 129.95; 128.81; 127.95; 120.21; 80.50; 28.21.

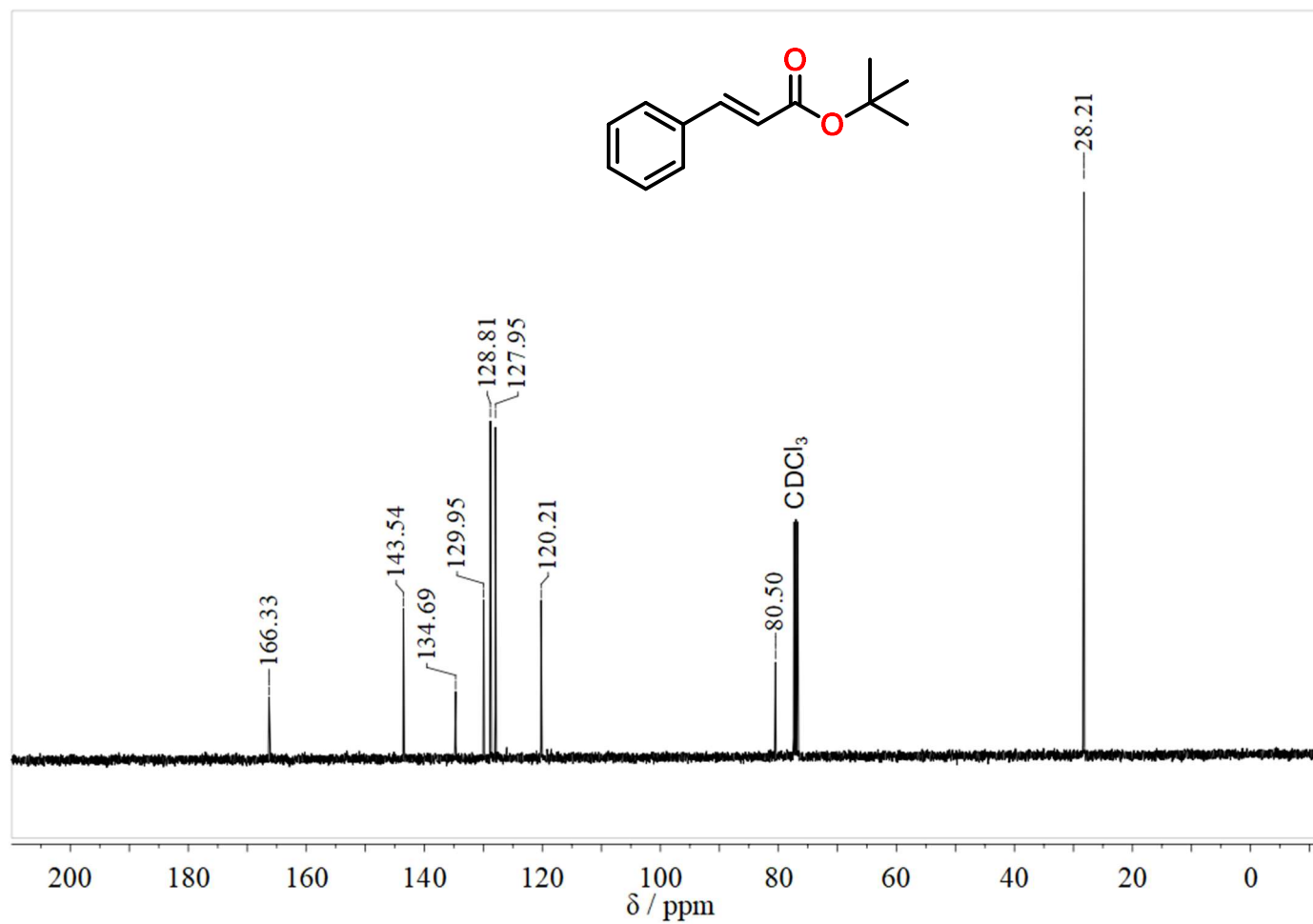


Figure S24. ^{13}C NMR (100 MHz) of ethyl-3-(4-methoxyphenyl)acrylate in CDCl_3 using tetramethylsilane (TMS) as internal standard. δ (ppm) 167.33; 161.34; 144.24; 129.68; 115.77; 114.31; 60.31; 55.35; 14.35.

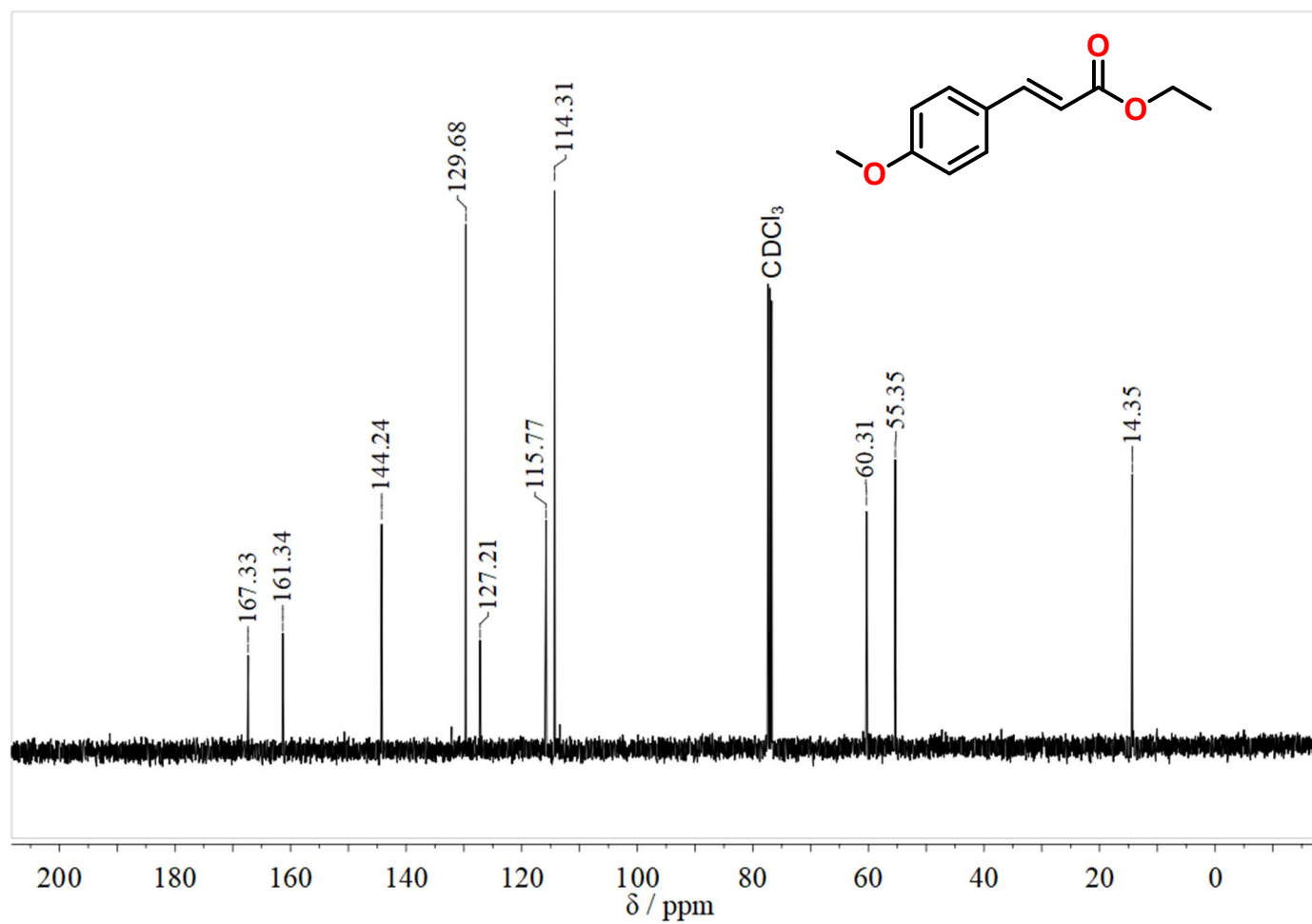


Figure S25. ^{13}C NMR (100 MHz) of ethyl-3-(4-acetylphenyl)acrylate in CDCl_3 using tetramethylsilane (TMS) as internal standard. δ (ppm) 197.31; 166.48; 142.99; 138.80; 137.97; 128.85; 128.11; 120.83; 60.76; 26.67; 14.29.

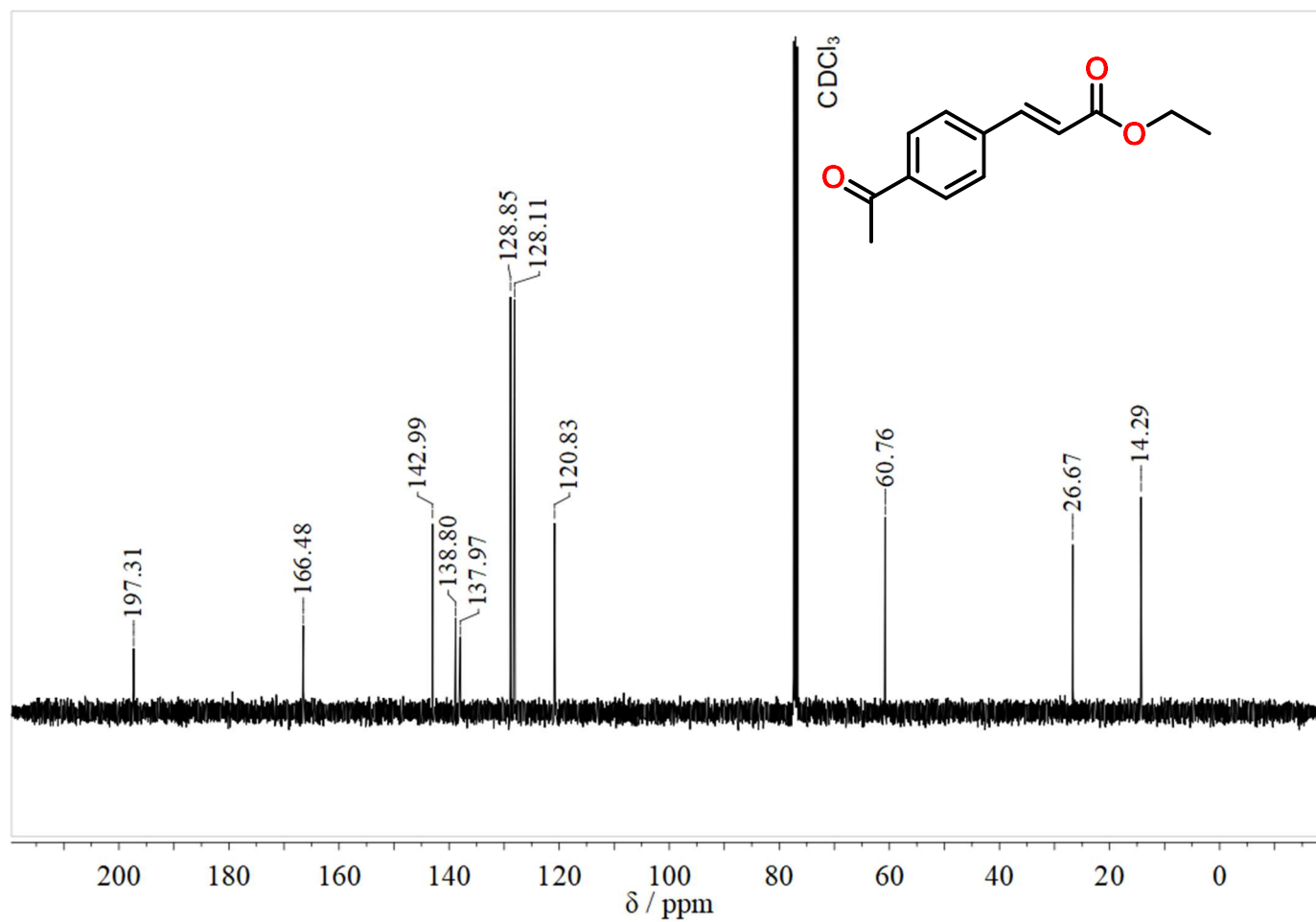


Figure S26. ^{13}C NMR (100 MHz) of ethyl-3-(4-nitrophenyl)acrylate in CDCl_3 using tetramethylsilane (TMS) as internal standard. δ (ppm) 166.02; 148.48; 141.60; 140.59; 128.61; 124.17; 122.60; 61.01; 14.25.

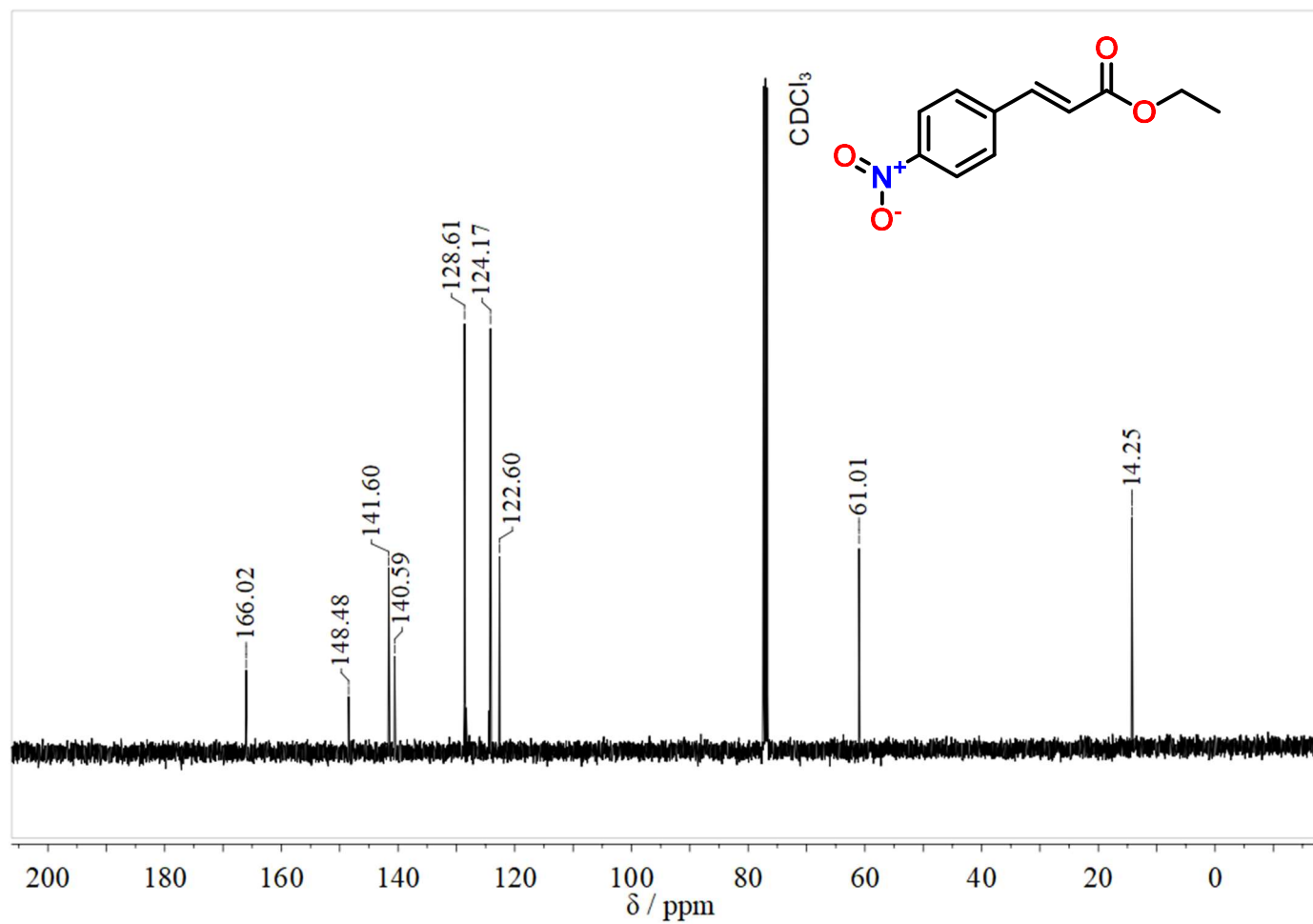


Figure S27. ^{13}C NMR (100 MHz) of ethyl-3-(2-methylphenyl)acrylate in CDCl_3 using tetramethylsilane (TMS) as internal standard. δ (ppm) 167.07; 142.29; 137.62; 133.46; 130.77; 129.95; 126.41; 126.32; 119.33; 60.48; 19.78; 14.34.

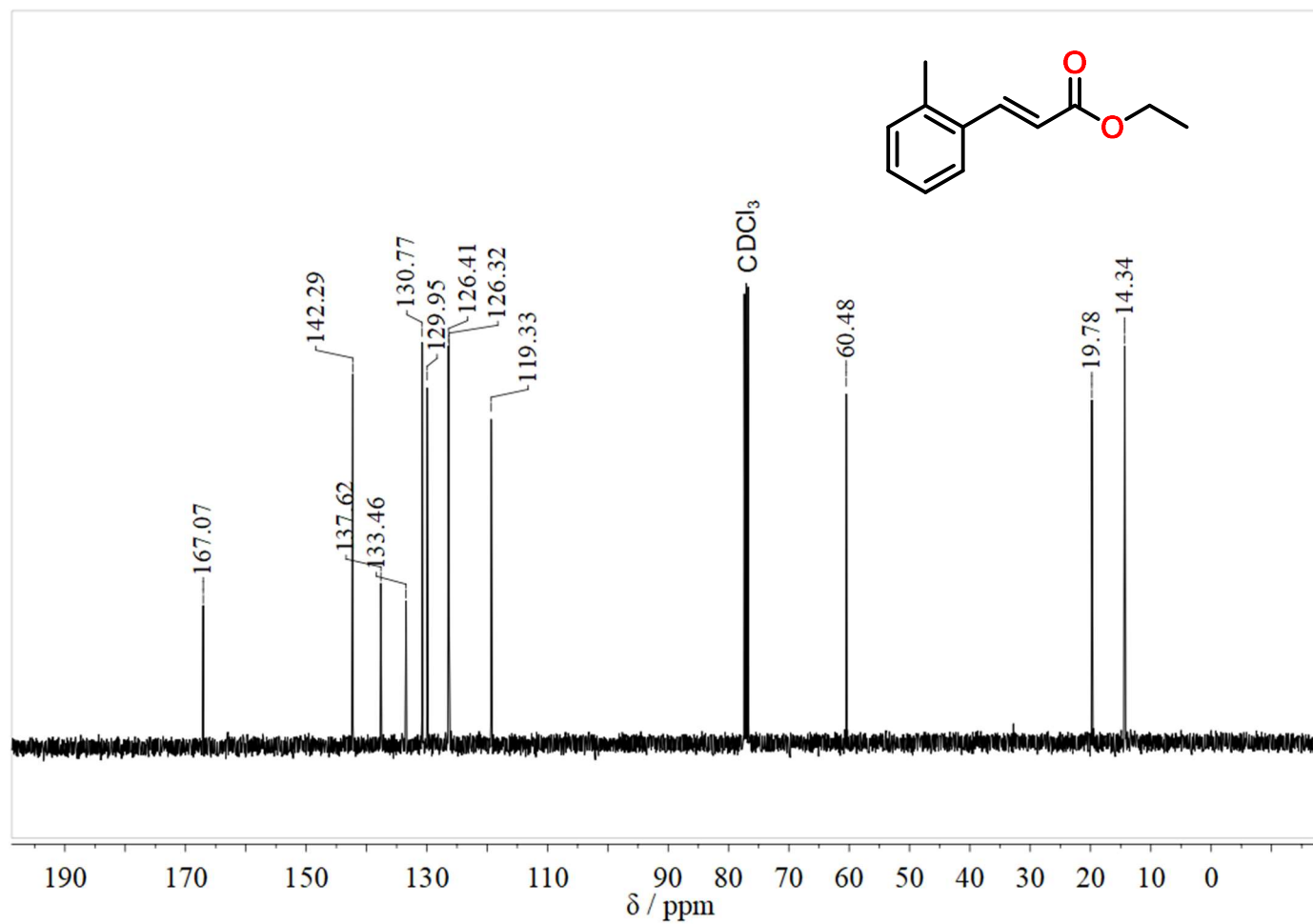


Figure S28. ^1H NMR (200MHz) of 4-methoxybiphenyl in CDCl_3 using tetramethylsilane (TMS) as internal standard. δ (ppm) 7.59 – 7.54 (m, 2H), 7.41 (t, $J = 7.3$ Hz, 3H), 6.97 (d, $J = 8.7$ Hz, 2H), 3.84 (s, 3H). The peaks at 3.76, 6.67 and 7.54 ppm are from 4-iodoanisole.

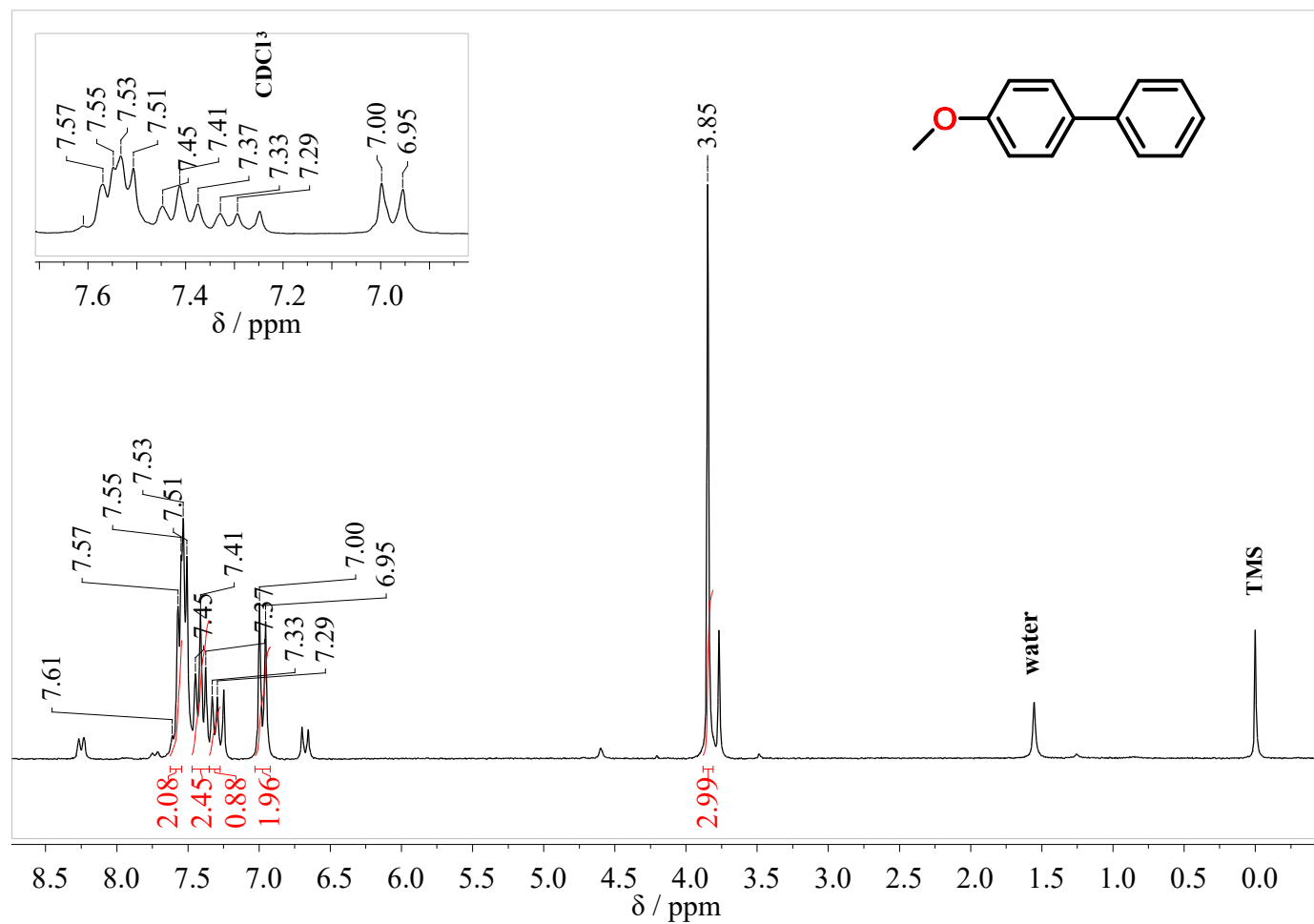


Figure S29. ^1H NMR (200MHz) of 4-acetylbiphenyl in CDCl_3 using tetramethylsilane (TMS) as internal standard. δ (ppm) 8.03 (d, $J = 8.5$ Hz, 2H), 7.68 (d, $J = 8.5$ Hz, 2H), 7.63 (d, $J = 7.8$ Hz, 2H), 7.53 – 7.37 (m, 3H), 2.64 (s, 3H).

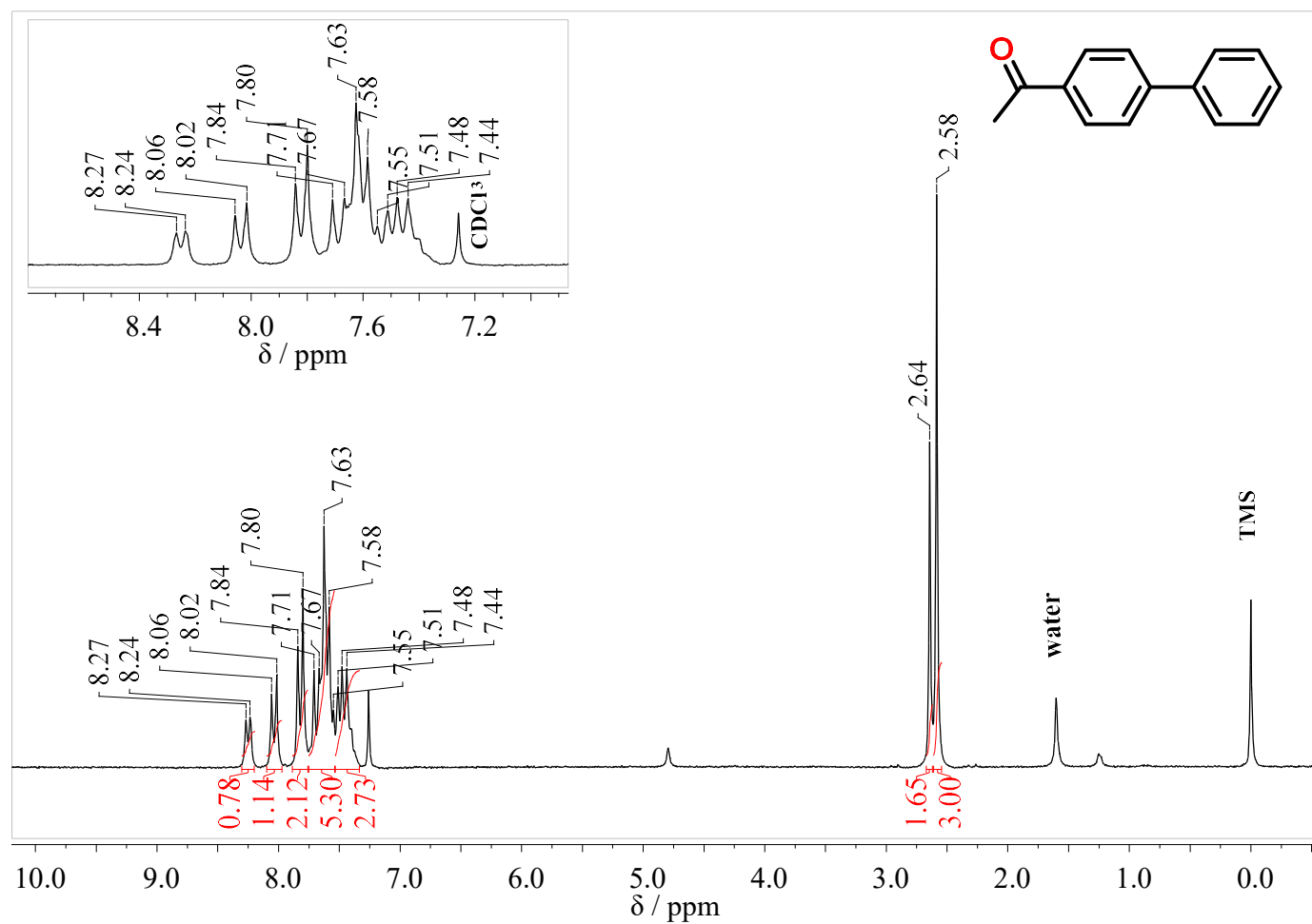


Figure S30. ^1H NMR (200MHz) of 4-hydroxybiphenyl in CDCl_3 using tetramethylsilane (TMS) as internal standard. δ (ppm) 7.72 – 7.17 (m, 7H), 6.90 (d, $J = 8.5$ Hz, 2H), 5.00 (s, 1H).

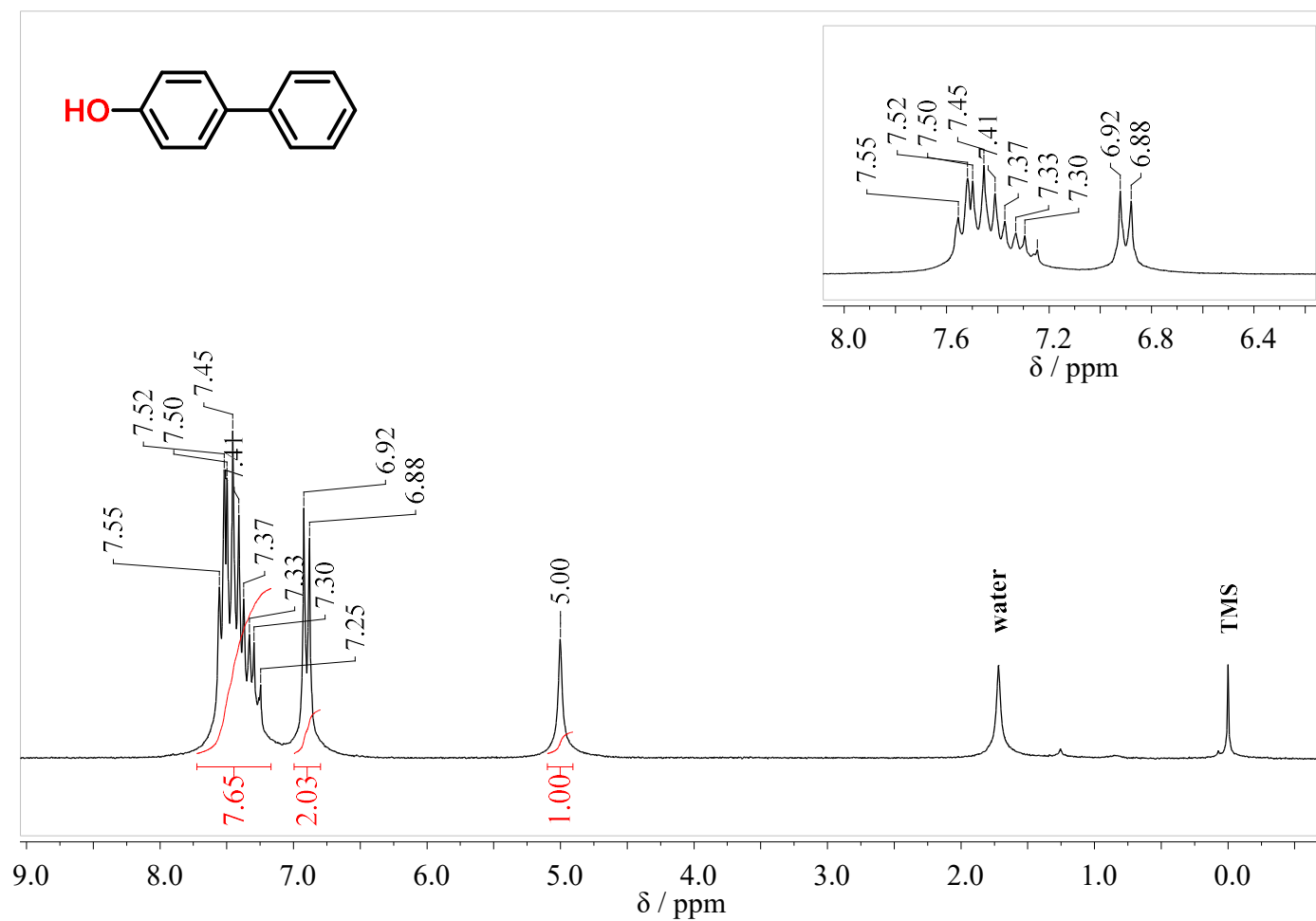


Figure S31 ^1H NMR (200MHz) of 4-aminobiphenyl in CDCl_3 using tetramethylsilane (TMS) as internal standard. δ (ppm) 7.55 (dd, $J = 7.2, 5.7$ Hz, 2H), 7.40 (dd, $J = 11.6, 4.9$ Hz, 5H), 7.32 – 7.17 (m, 2H), 6.80 – 6.70 (m, 2H), 3.68 (s, 1H).

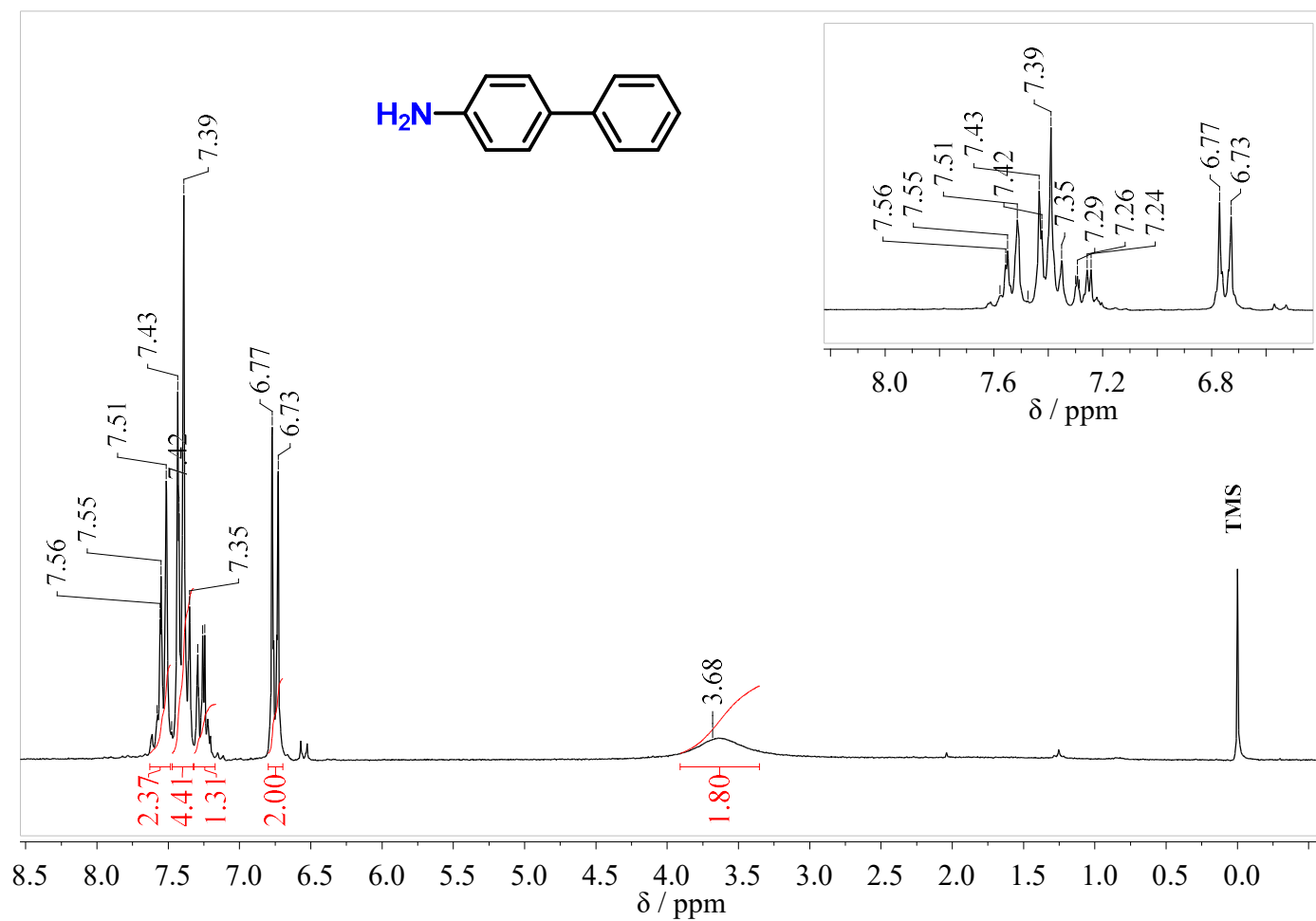


Figure S32. ^1H NMR (200MHz) of 2-methylbiphenyl in CDCl_3 using tetramethylsilane (TMS) as internal standard. δ 7.31 (ddd, $J = 15.8, 7.5, 4.5$ Hz, 9H), 2.27 (s, 3H).

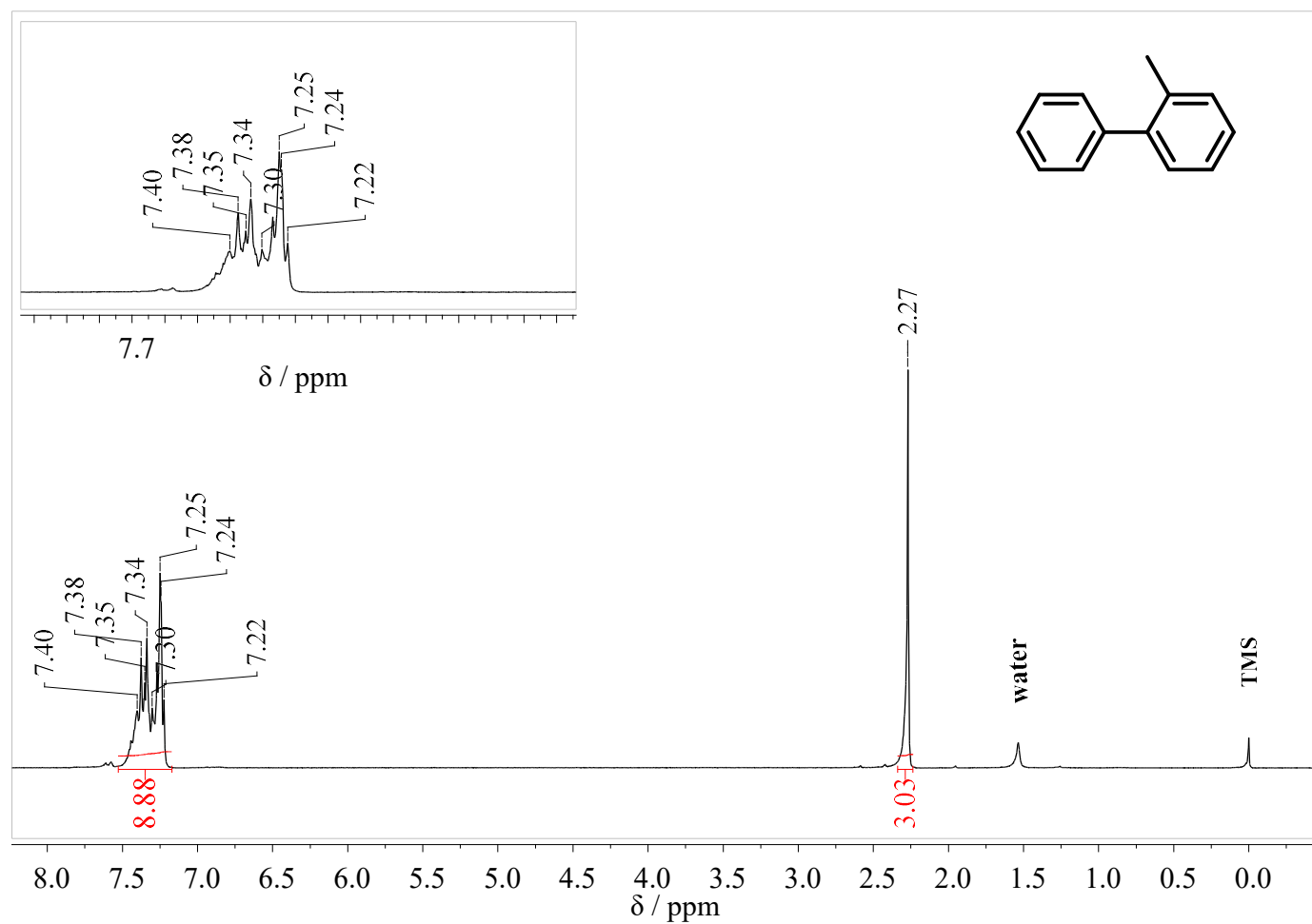


Figure S33. ^1H NMR of biphenyl in CDCl_3 (10-fold reaction scale). δ (ppm) 7.59 (d, $J = 6.9$ Hz, 4H), 7.44 (t, $J = 7.2$ Hz, 4H), 7.38–7.27 (m, 2H). The peaks at 4.64 and 8.25 ppm are from monomer and dimer from the phenylboronic acid (starting material), respectively.

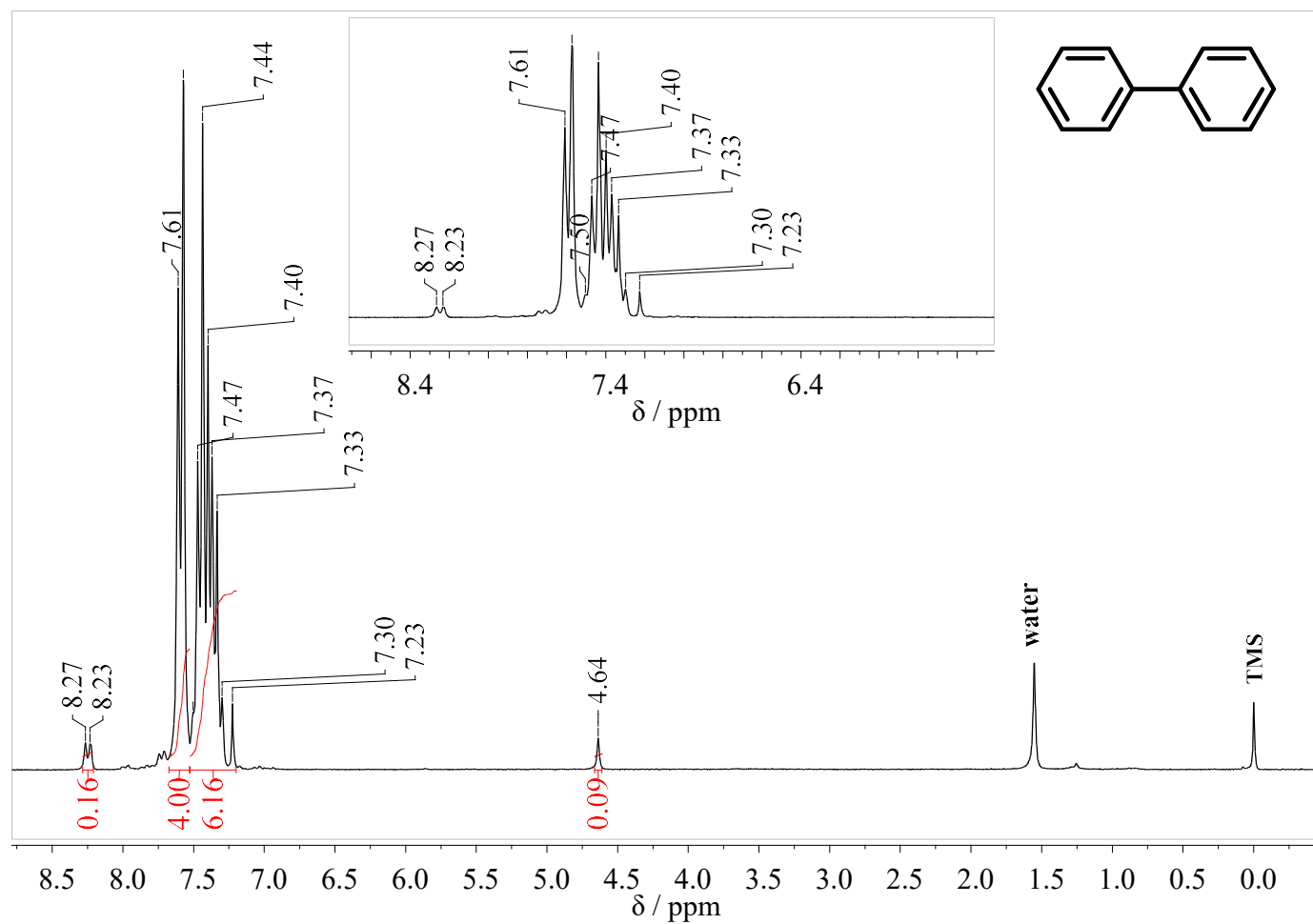


Figure S34. ^{13}C NMR (100MHz) of 4-methoxybiphenyl in CDCl_3 using tetramethylsilane (TMS) as internal standard. δ (ppm) 159.19; 140.86; 133.82; 128.76; 128.19; 126.77; 126.69; 114.25; 55.36.

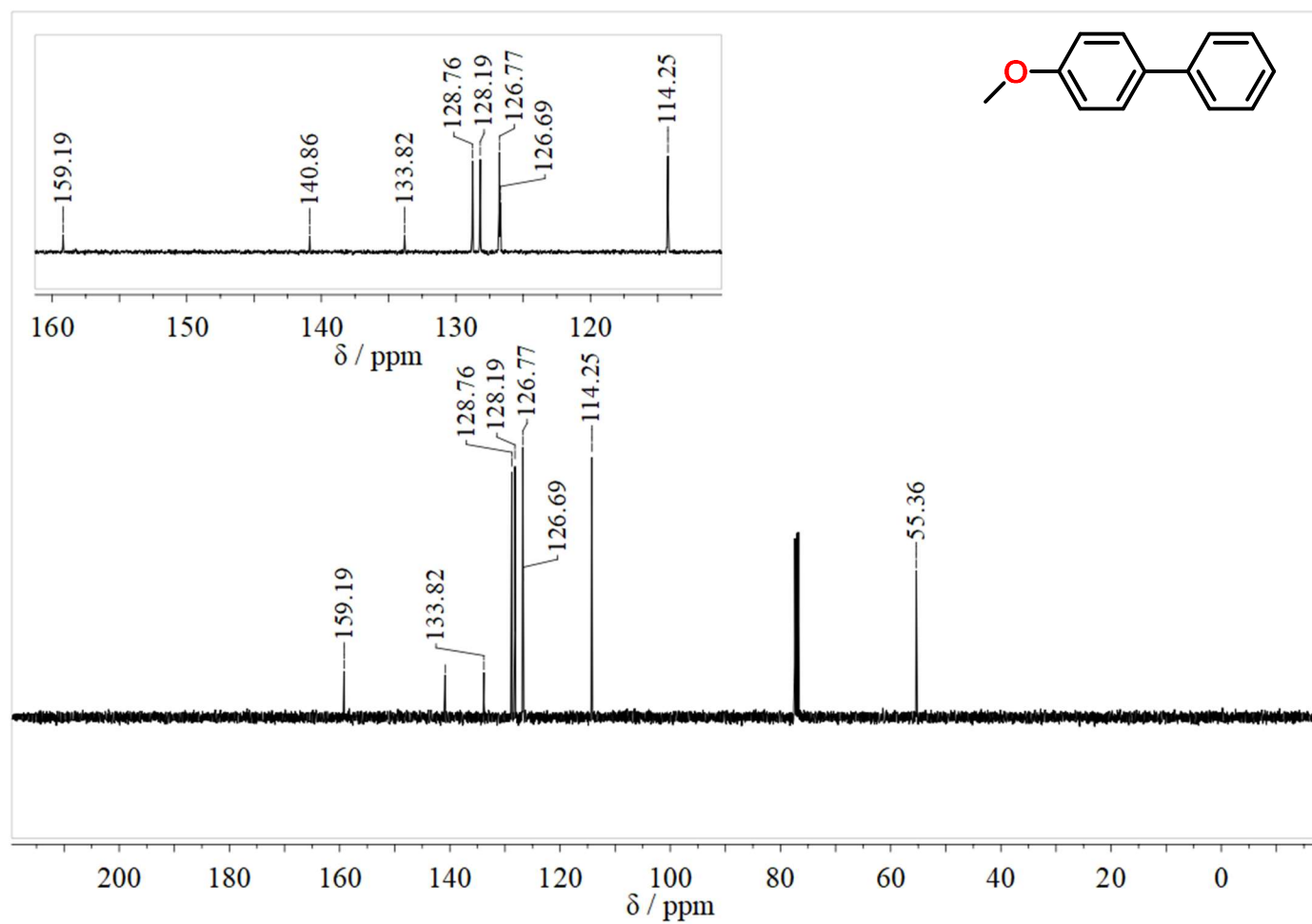


Figure S35. ^{13}C NMR (100MHz) of 4-acetylbiphenyl in CDCl_3 using tetramethylsilane (TMS) as internal standard. δ (ppm) 145.79; 139.87; 135.87; 128.98; 128.94; 128.26; 127.28; 127.23; 26.66.

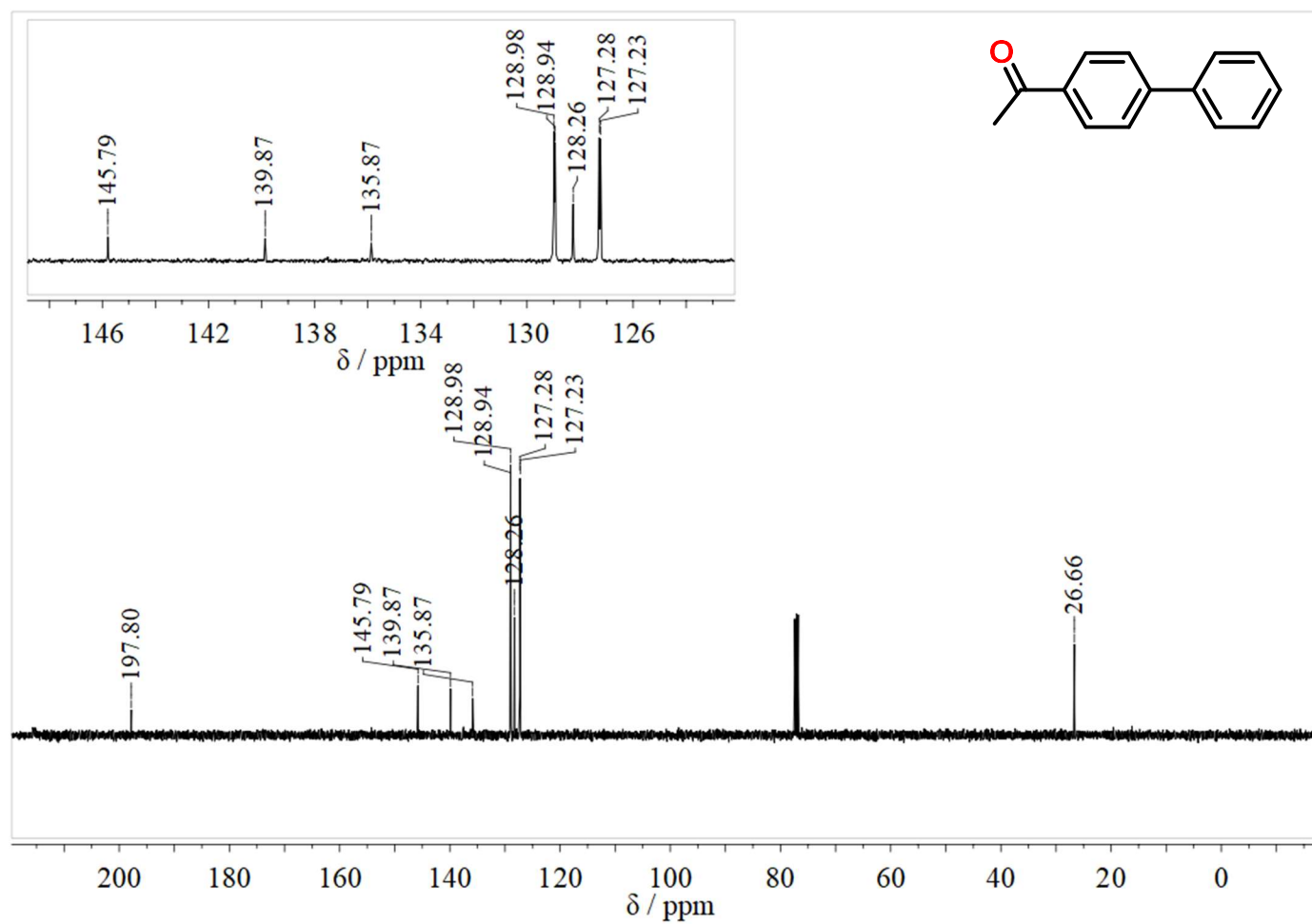


Figure S36. ^{13}C NMR (100MHz) of 4-hydroxybiphenyl in CDCl_3 using tetramethylsilane (TMS) as internal standard. δ (ppm) 155.10; 140.77; 134.04; 128.74; 128.41; 126.73; 115.66.

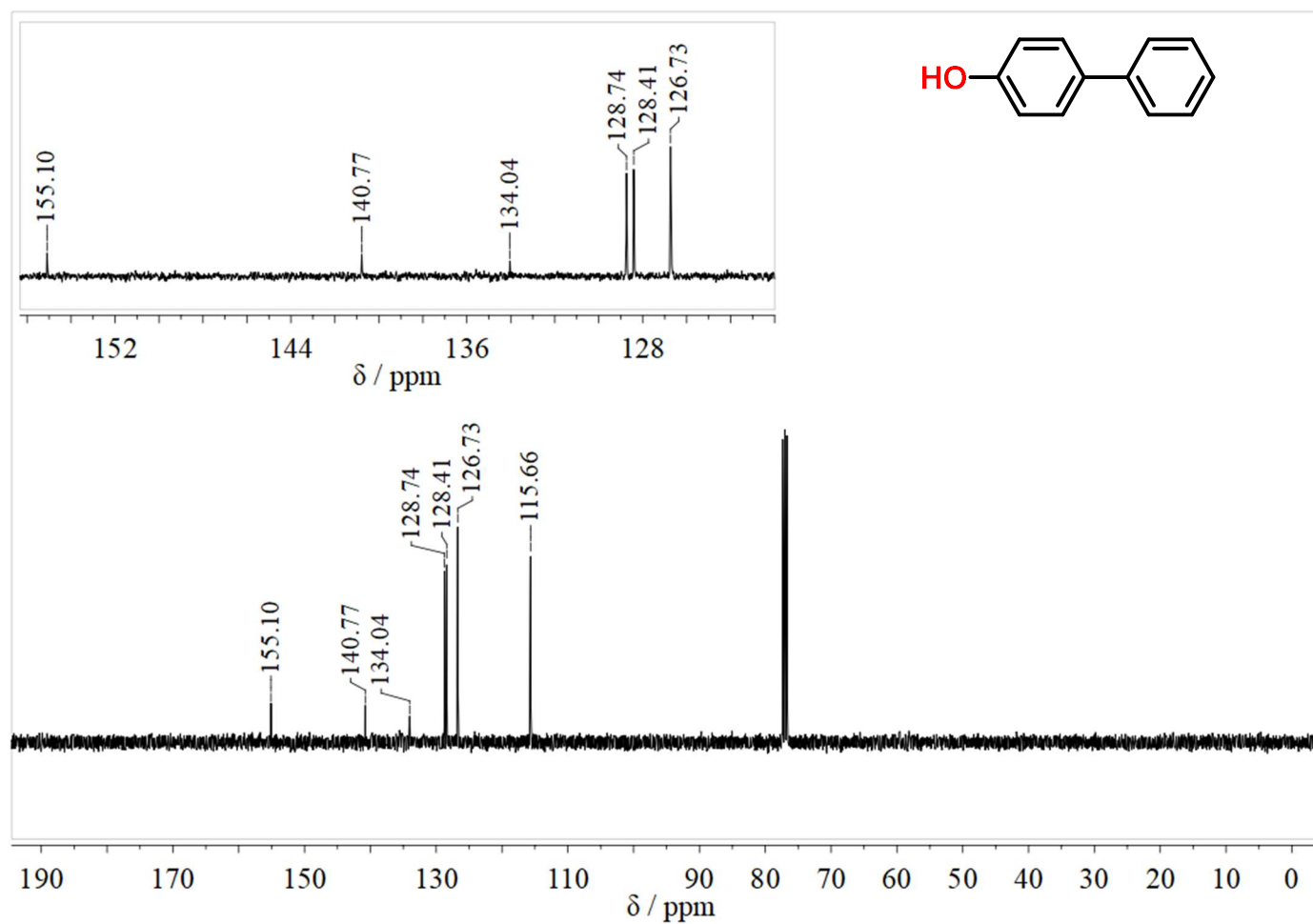


Figure S37. ^{13}C NMR (100MHz) of 2-methylbiphenyl in CDCl_3 using tetramethylsilane (TMS) as internal standard. δ (ppm) 141.99; 135.70; 135.38; 132.74; 130.34; 129.84; 129.23; 128.10; 128.04; 127.29; 126.80; 125.80.

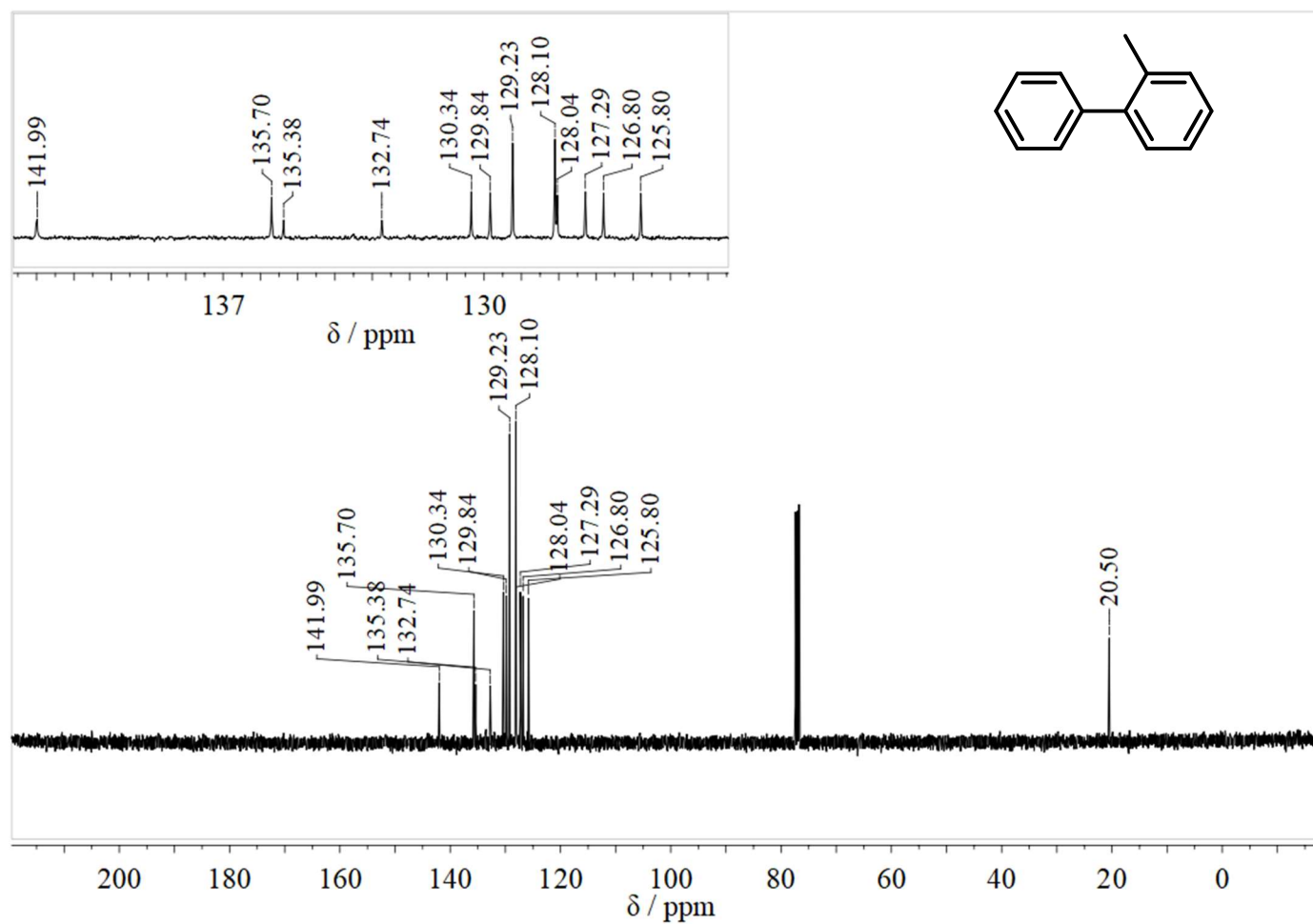


Figure S38. ^{13}C NMR (200MHz) of 4-aminobiphenyl in CDCl_3 using tetramethylsilane (TMS) as internal standard. δ (ppm) 145.91; 141.22; 131.60; 128.73; 128.05; 127.22; 126.45; 126.31; 115.46.

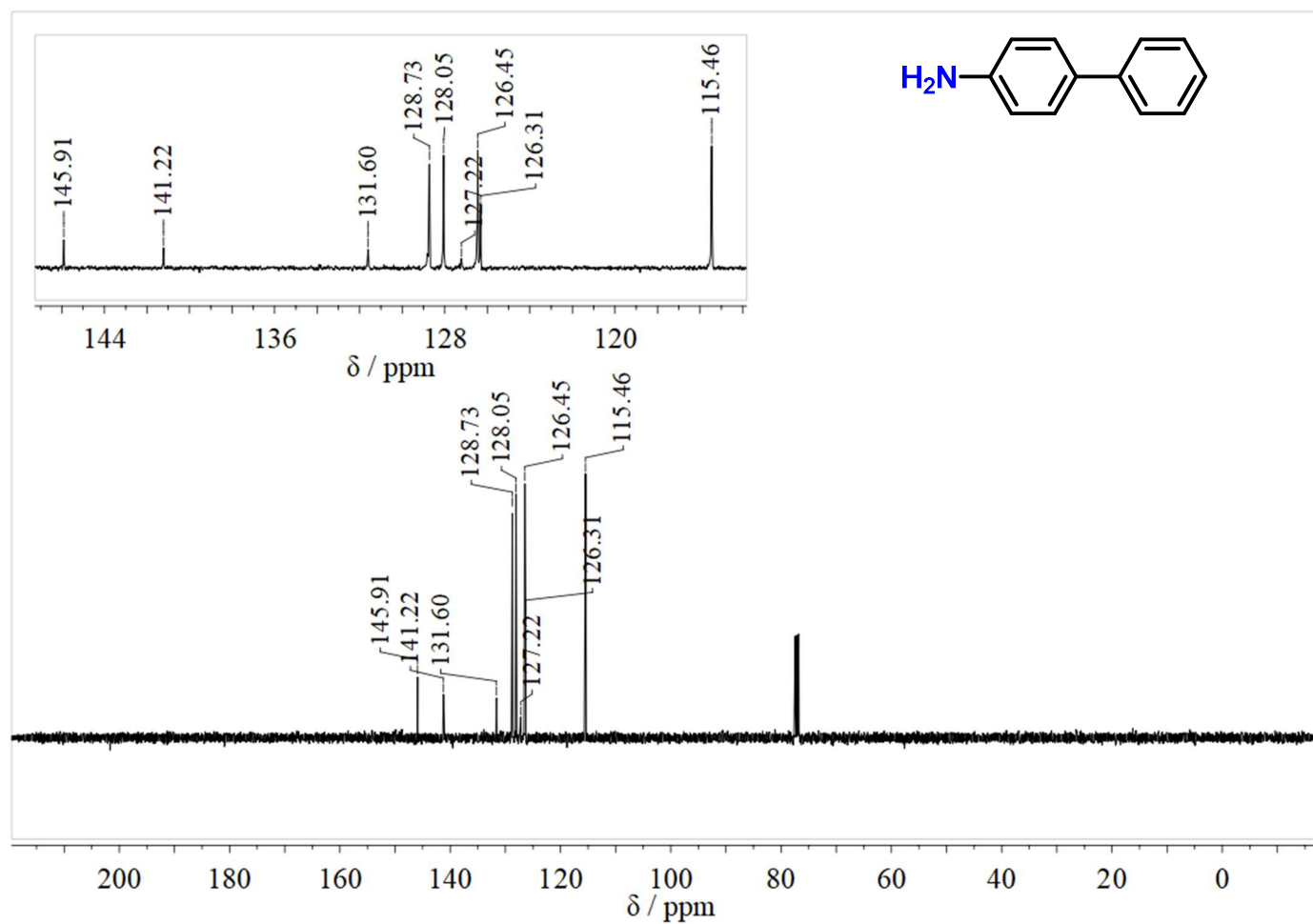


Figure S39. ^{13}C NMR of biphenyl in CDCl_3 (10-fold reaction scale). δ (ppm) 135.65; 133.46; 132.71; 128.00.

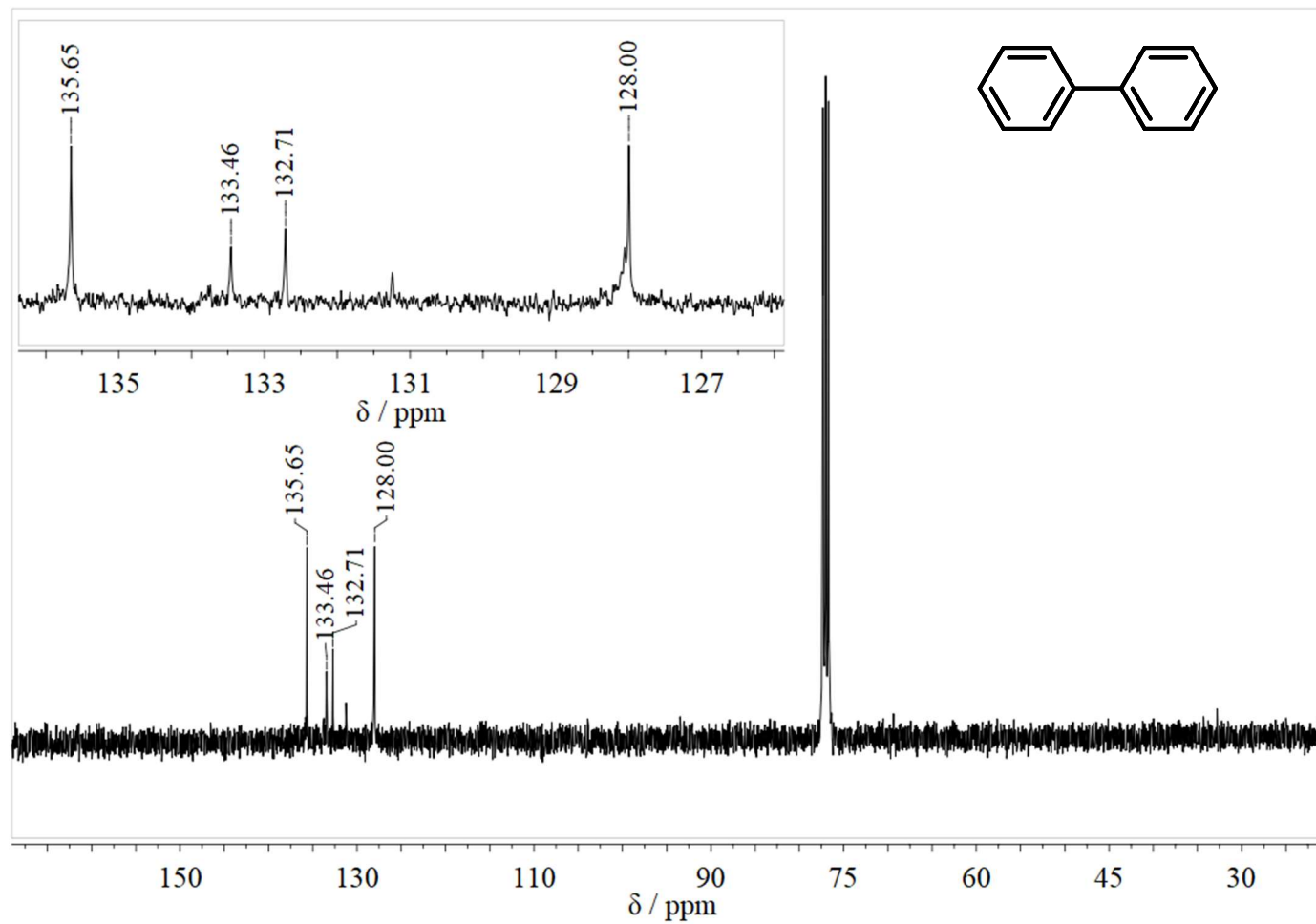


Figure S40. Calibration curves from (a) ethyl cinnamate, (b) iodobenzene and (c) biphenyl.

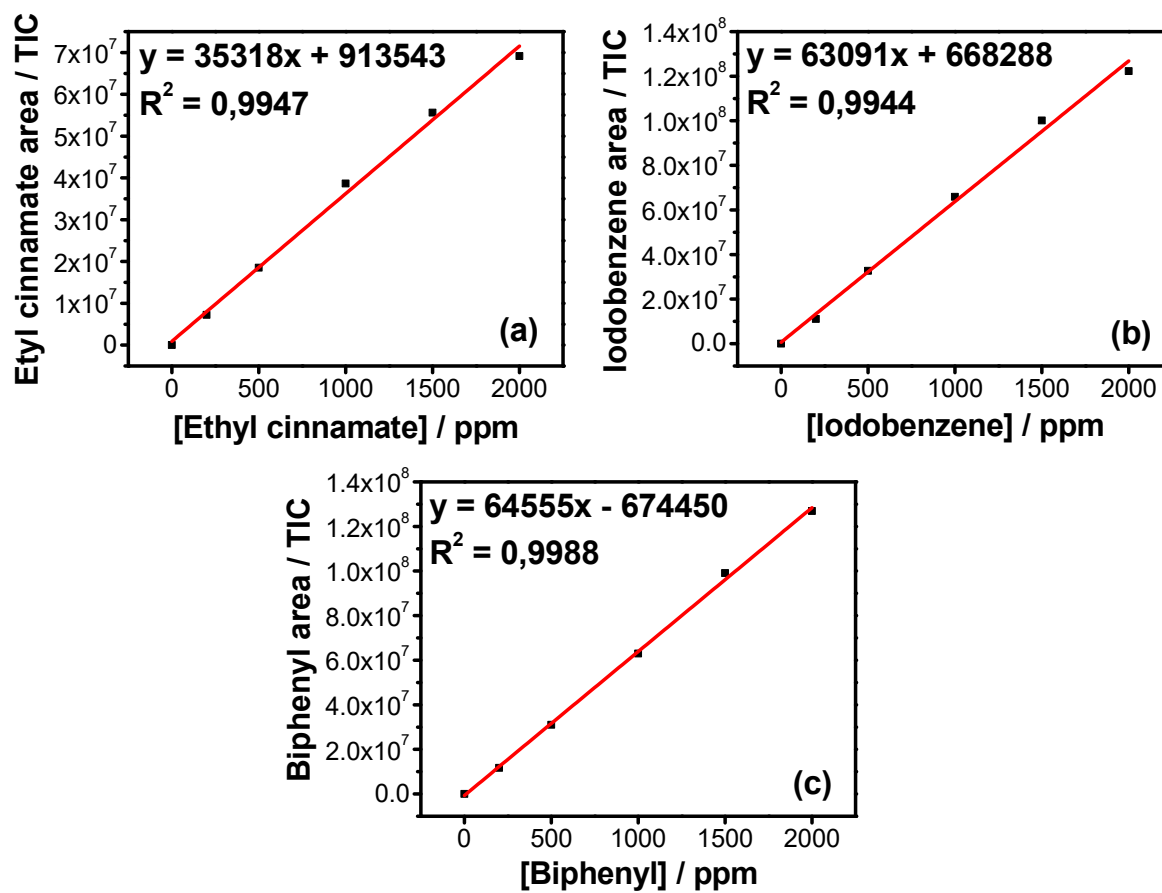


Figure S41. Chromatogram and mass fragmentogram of iodobenzene ($t_r = 7.00$ min) and ethyl cinnamate ($t_r = 9.95$ min). Decane ($t_r = 6.50$ min) was used as internal standard.

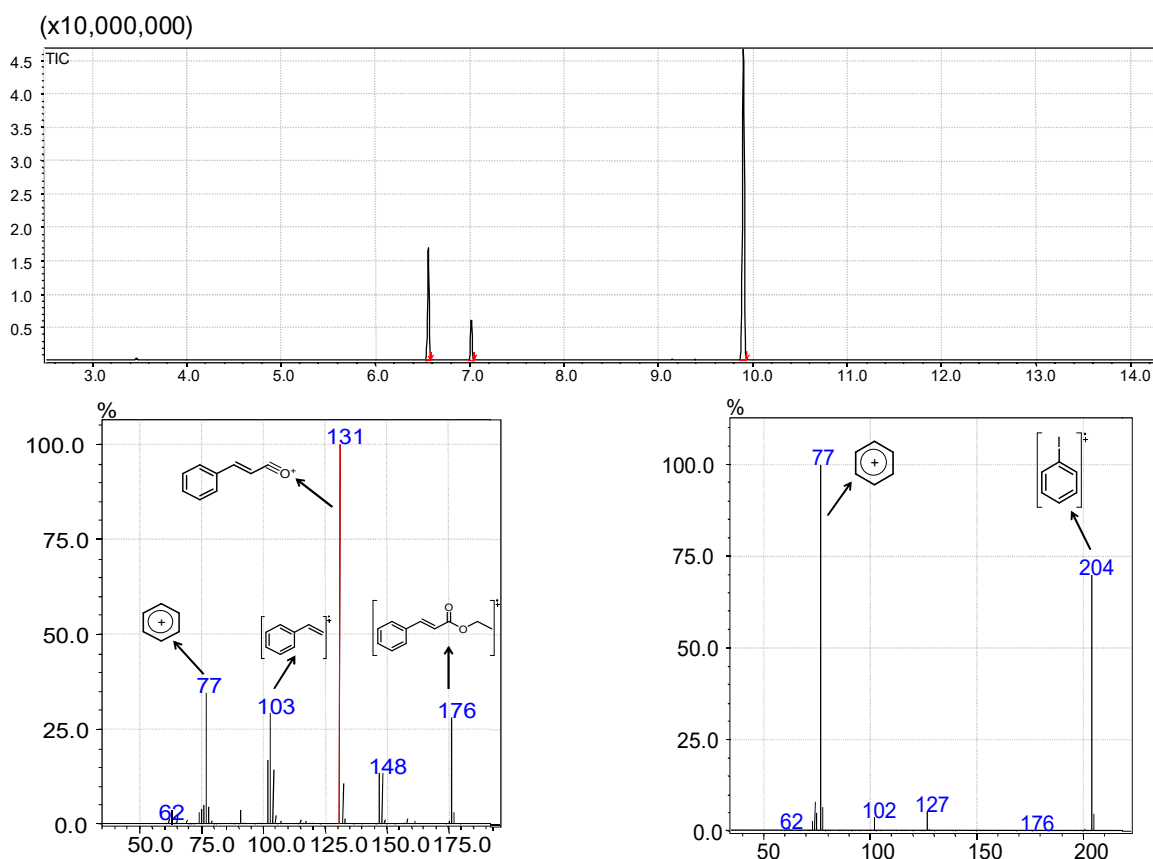


Figure S42. Chromatogram and mass fragmentogram of iodobenzene ($t_r = 7.425$ min) and biphenyl ($t_r = 9.562$ min). Decane ($t_r = 6.99$ min) was used as internal standard.

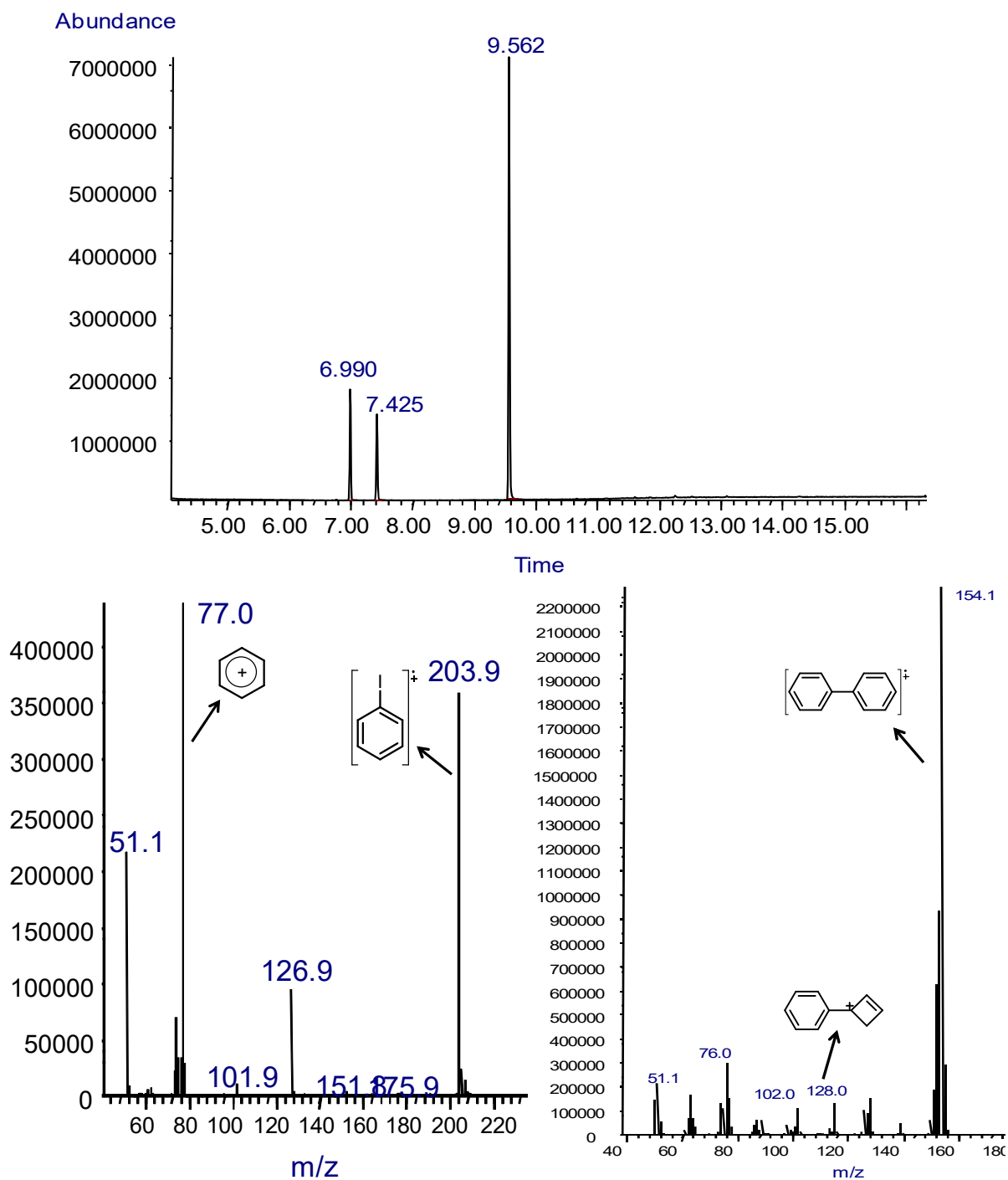


Figure S43. LC/MS-QTOF mass spectra (positive mode) of 3-(1-(2-butyloctyl)-3-imidazolium)propanesulfonate – ImS3b-4 in methanol containing 0.1 % formic acid.

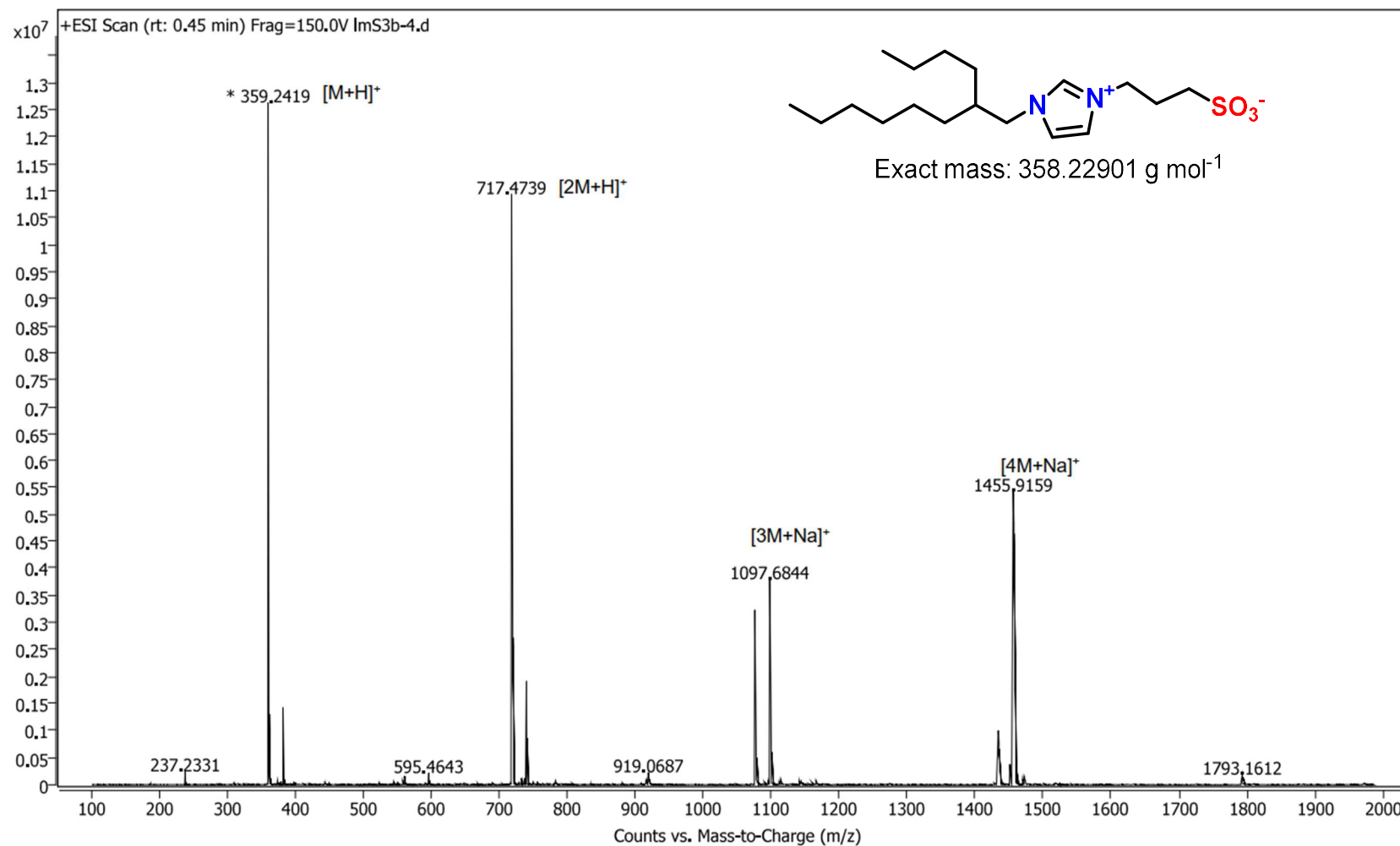


Figure S44. LC/MS-QTOF mass spectra (positive mode) of 3-(1-(2-hexyldecyl)-3-imidazolium)propanesulfonate – ImS3b-6 in methanol containing 0.1 % formic acid.

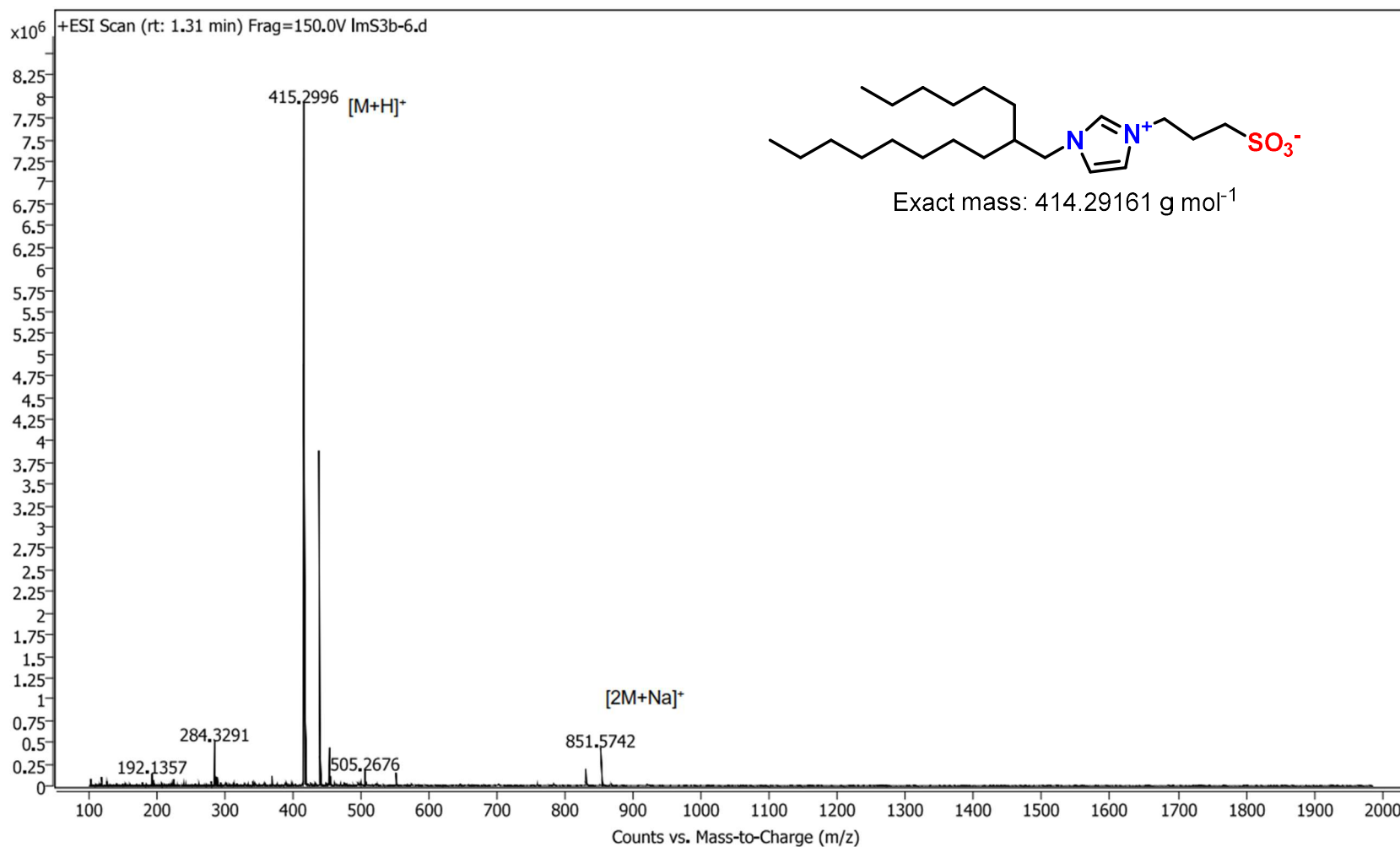


Figure S45 LC/MS-QTOF mass spectra (positive mode) of 3-(1-(2-octyldodecyl)-3-imidazolium)propanesulfonate – ImS3b-8 in methanol containing 0.1 % formic acid.

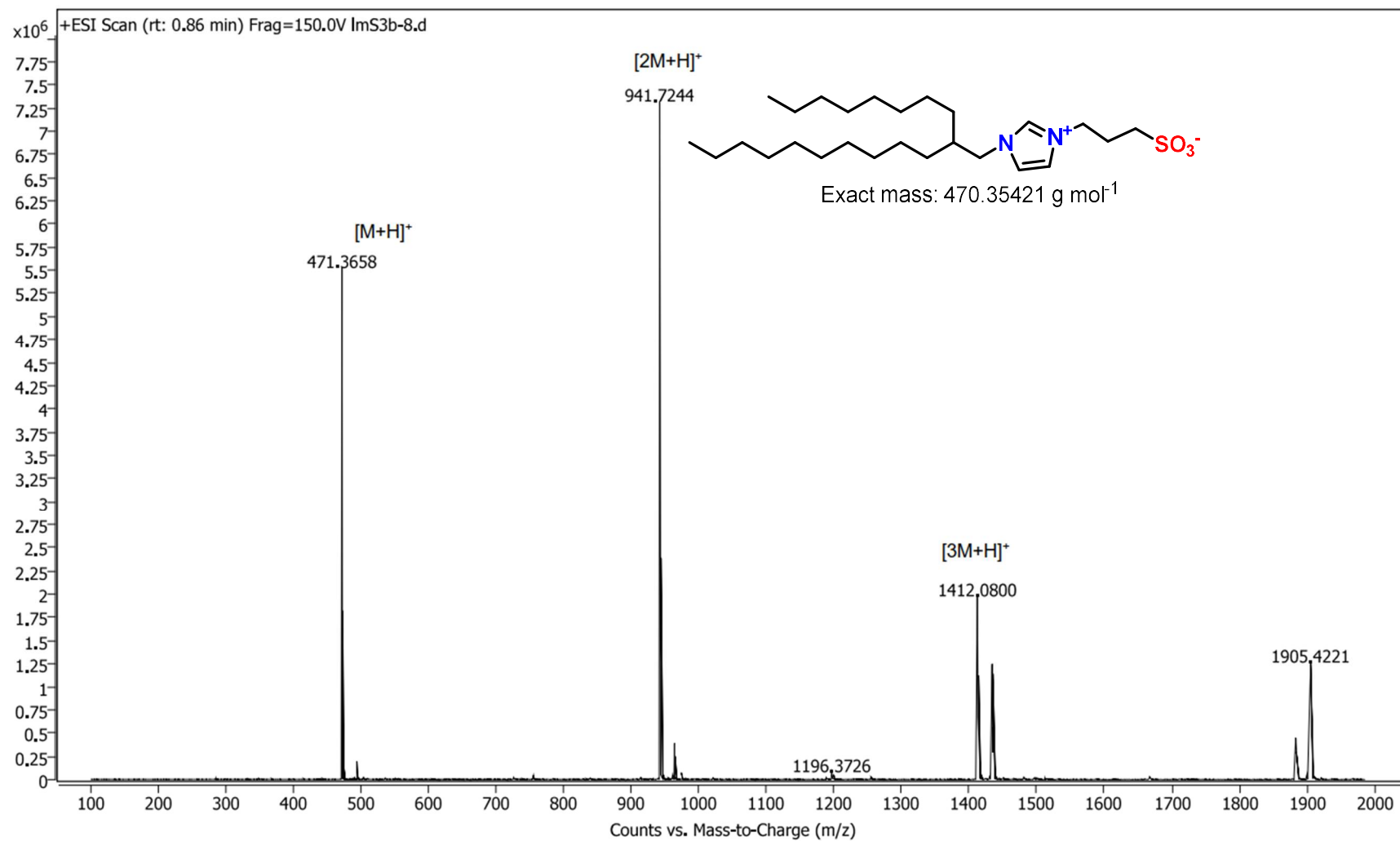
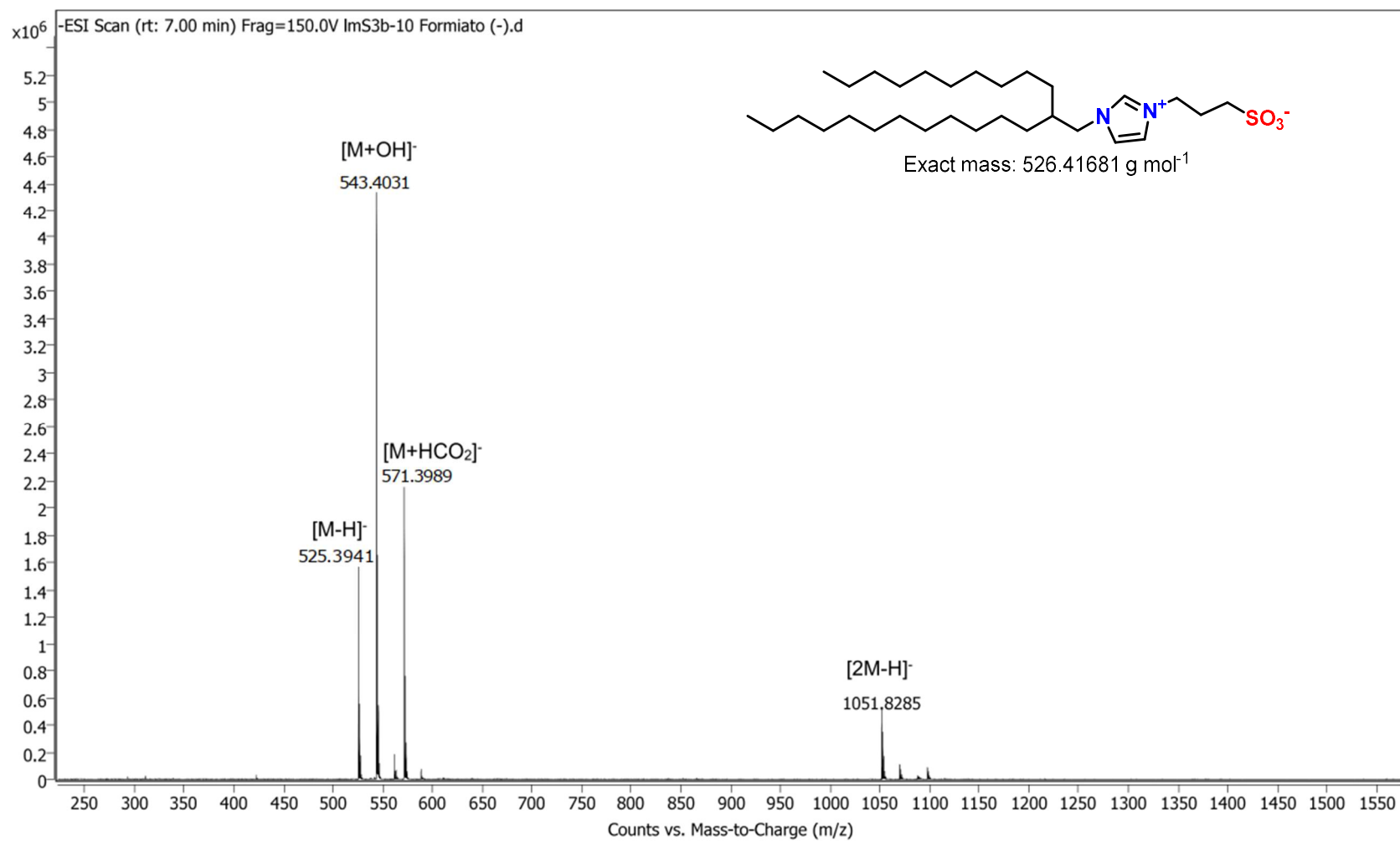


Figure S46. LC/MS-QTOF mass spectra (negative mode) of 3-(1-(2-decyltetradecyl)-3-imidazolium)propanesulfonate – ImS3b-10 in methanol containing 0.1 % ammonium formate.



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