Diversity Oriented Metal Decoration on UiO-Type Metal-Organic Frameworks: an Efficient Approach to Increase CO_2 Uptake and Catalytic Conversion to Cyclic Carbonates

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Contents

Contents	Page
Experimental Details	S1
Figure S1. PXRD patterns of metal-grafted Bipy-UiO-67 MOFs.	S6
Figure S2-S23-.NMR spectrum for data reported in Table 1.	S7-S28
Figure S24-S32-.NMR spectrum for data reported in Table 2.	S29-S37
Figure S33-S42-.NMR spectrum for data reported in Table 4.	S38-S47
Figure S43-S47-.NMR spectra of recyclability tests.	S78-S52

Experimental Details, Representative Procedure for the Cyclic Carbonate Formation:


R = CH₂Cl,
  phenyl,
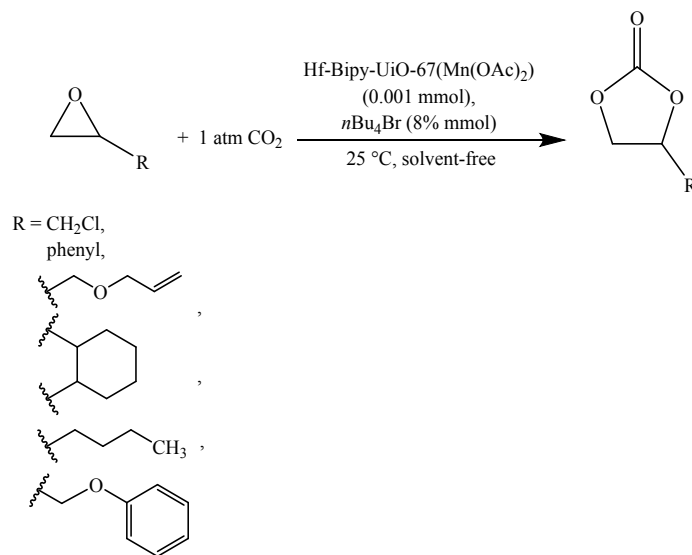
4-(chloromethyl)-1,3-dioxolan-2-one
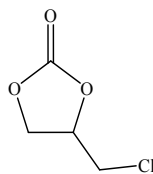
In a 20 mL glass reactor, epichlorohydrin (4.3 mmol, 0.397 mL), Hf-Bipy-UiO-67(Mn(OAc)$_2$) (0.001 mmol, 0.012 g), nBu$_4$Br (8% mmol, 0.11 g) were added with a magnetic stirring bar. Then, the reactor was flushed under 1 bar pressure of CO$_2$ at room temperature for 12h. After completion, the reaction mixture was analyzed by ^{1}H NMR (yield: 99%).

^{1}H NMR (300 MHz, CDCl$_3$): 3.73-3.85 (2H, m, CH$_2$—Cl), 4.43 (1H, dd, $^2J_{HH}$ = 15 Hz, $^3J_{HH}$ = 6 Hz, O—CH$_2$), 4.65 (1H, dd, $^2J_{HH}$ = 15 Hz, $^3J_{HH}$ = 9 Hz, O—CH$_2$) and 5.04 (1H, m, O—CH). ^{13}C NMR (75 MHz, CDCl$_3$): 44.1 (CH$_2$—Cl), 67.2 (O—CH$_2$), 74.0 (O—CH) and 153.8 (C=O).
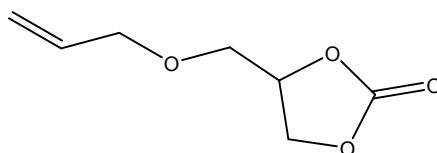
4-phenyl-1,3-dioxolan-2-one

S3
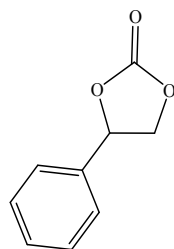
In a 20 mL glass reactor, styrene oxide (4.3 mmol, 0.516 mL), Hf-Bipy-UiO-67(Mn(OAc)$_2$) (0.001 mmol, 0.012 g), nBu$_4$Br (8% mmol, 0.11 g) were added with a magnetic stirring bar. Then, the reactor was flushed under 1 bar pressure of CO_2 at 50 °C for 4h. After completion, the reaction mixture was analyzed by ^{1}H NMR (yield: >99%).

^{1}H NMR (300 MHz, CDCl$_3$): 4.34 (1H, dd, $^2J_{HH}$ = 9 Hz, $^3J_{HH}$ = 6 Hz, O—CH$_2$), 4.83 (1H, dd, $^2J_{HH}$ = 6 Hz, $^3J_{HH}$ = 3 Hz, O—CH$_2$), 5.68-5.64 (1H, m, O—CH) and 7.35-7.43 (5H, m, Ph). ^{13}C NMR (75 MHz, CDCl$_3$): 71.1 (O—CH$_2$), 74.2 (O—CH), 122.6, 128.6, 129.9 (CH of Ph), 135.6 (C$_{ipso}$) and 158.6 (C=O).

4-((allyloxy)methyl)-1,3-dioxolan-2-one

In a 20 mL glass reactor, allyl glycidyl ether (4.3 mmol, 0.490 mL), Hf-Bipy-UiO-67(Mn(OAc)$_2$) (0.001 mmol, 0.012 g), nBu$_4$Br (8% mmol, 0.11 g) were added with a magnetic stirring bar. Then, the reactor was flushed under 1 bar pressure of CO_2 at 50 °C for 4h. After completion, the reaction mixture was analyzed by ^{1}H NMR (yield: >99%).

^{1}H NMR (300 MHz, CDCl$_3$): 3.71-3.72 (2H, m, O—CH$_2$), 3.99-4.40 (2H, m, O—CH$_2$), 4.37-4.65 (2H, m, O—CH$_2$), 4.82-4.88 (1H, m, CH of allyl), 5.19-5.30 (2H, m, CH of allyl) and 5.79-5.92 (1H, m, O—CH). ^{13}C NMR (75 MHz, CDCl$_3$): 155.2, 133.9, 117.3, 75.4, 72.3, 68.9, 66.2.

hexahydrobenzo[d][1,3]dioxol-2-one
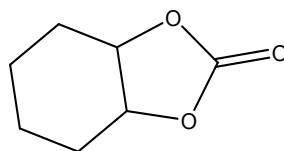
In a 20 mL glass reactor, 7-oxabicyclo[4.1.0]heptane (4.3 mmol, 0.422 mL), Hf-Bipy-UiO-67(Mn(OAc)$_2$) (0.012 mmol, 0.006 g), nBu$_4$Br (8% mmol, 0.11 g) were added with a magnetic stirring bar. Then, the reactor was flushed under 1 bar pressure of CO_2 at 50 °C for 4h. After completion, the reaction mixture was analyzed by ^{1}H NMR (yield: >99%).

^{1}H NMR (300 MHz, CDCl$_3$): 1.61-1.72 (4H, m, 2CH$_2$), 1.82-1.96 (4H, m, 2CH$_2$) and 4.67-4.69 (2H, m, 2CH). ^{13}C NMR (75 MHz, CDCl$_3$): 19.2 (2CH$_2$), 26.3 (2CH$_2$), 75.4 (2CH) and 158.6 (C=O).
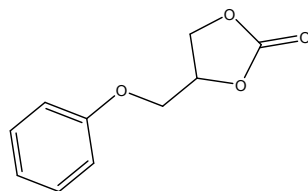
4-butyl-1,3-dioxolan-2-one
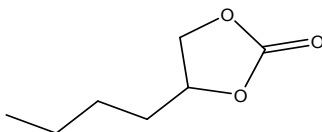
In a 20 mL glass reactor, (S)-2-butyloxirane (4.3 mmol, 0.430 mL), Hf-Bipy-UiO-67(Mn(OAc)$_2$) (0.001 mmol, 0.012 g), nBu$_4$Br (8% mmol, 0.11 g) were added with a magnetic stirring bar. Then, the reactor was flushed under 1 bar pressure of CO$_2$ at 50 °C for 4h. After completion, the reaction mixture was analyzed by ^{1}H NMR (yield: 95%).

^{1}H NMR (300 MHz, CDCl$_3$): 0.89-99 (3H, m, CH$_3$), 1.32-1.45 (4H, m, 2CH$_2$), 1.61-1.64 (2H, m, CH$_2$), 4.05 (1H, t, $^3J_{HH}$ = 9 Hz, O—CH), 4.53 (1H, dd, $^2J_{HH}$ = 9 Hz, $^3J_{HH}$ = 6 Hz, O—CH$_2$) and 4.65-4.68 (1H, m, O—CH$_2$). ^{13}C NMR (75 MHz, CDCl$_3$): 13.3 (CH$_3$), 21.4, 27.9, 37.5 (3CH$_2$), 66.1 (O—CH$_2$), 75.3 (O—CH) and 155.6 (C=O).

4-(phenoxymethyl)-1,3-dioxolan-2-one

In a 20 mL glass reactor, 1,2-Epoxy-3-phenoxy propane (4.3 mmol, 0.645 mL), Hf-Bipy-UiO-67(Mn(OAc)$_2$) (0.001 mmol, 0.012 g), nBu$_4$Br (8% mmol, 0.11 g) were added with a magnetic stirring bar. Then, the reactor was flushed under 1 bar pressure of CO$_2$ at 50 °C for 4h. After completion, the reaction mixture was analyzed by ^{1}H NMR (yield: 95%).

^{1}H NMR (300 MHz, CDCl$_3$): 4.08-4.29 (2H, m, O—CH$_2$), 4.54-4.68 (2H, m, O—CH$_2$), 5.07 (2H, m, O—CH), 6.93 (2H, d, $^3J_{HH}$ = 6 Hz, 2CH$_{ortho}$ of Ph), 7.04 (1H, t, $^3J_{HH}$ = 9 Hz, CH$_{para}$ of Ph) and 7.33 (2H, t, $^3J_{HH}$ = 9 Hz, 2CH$_{meta}$ of Ph). ^{13}C NMR (75 MHz, CDCl$_3$): 66.3 (O—CH$_2$), 67.4 (O—CH), 74.5 (O—CH$_2$), 114,5, 121.7, 129.3 (3CH of Ph), 154.4 (C$_{ipso}$) and 157.8 (C=O).

Figure S1. PXRD patterns of metal-grafted Bipy-UiO-67 MOFs.

The figure shows PXRD patterns labeled (top to bottom): Hf-Bipy-MnCl$_2$, Hf-Bipy-CoCl$_2$, Hf-Bipy- CuCl$_2$, Hf-Bipy-ZnCl$_2$, Zr-Bipy-MnCl$_2$, Zr-Bipy- CuCl$_2$, Hf-Bipy- Co(OAC)$_2$, Hf-Bipy- Cu(OAC)$_2$, Hf-Bipy- Zn(OAC)$_2$, Zr-Bipy-Mn(OAC)$_2$, Zr-Bipy- Cu(OAC)$_2$, Hf-Bipy-Mn(NO$_3$)$_2$, Hf-Bipy- Co(NO$_3$)$_2$, Hf-Bipy- Cu(NO$_3$)$_2$, Hf-Bipy- Zn(NO$_3$)$_2$. The x-axis is 2θ/° ranging from 5 to 40.
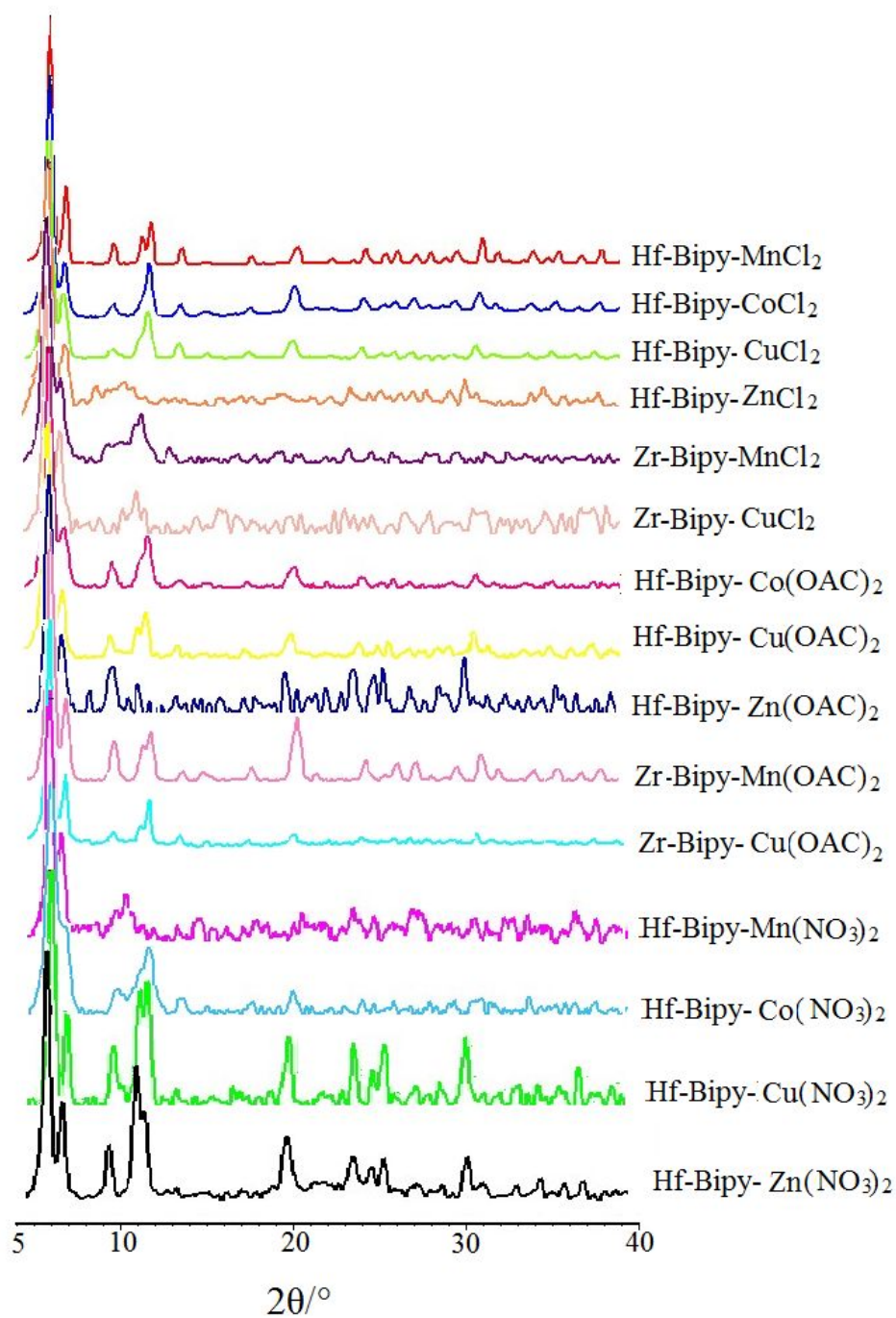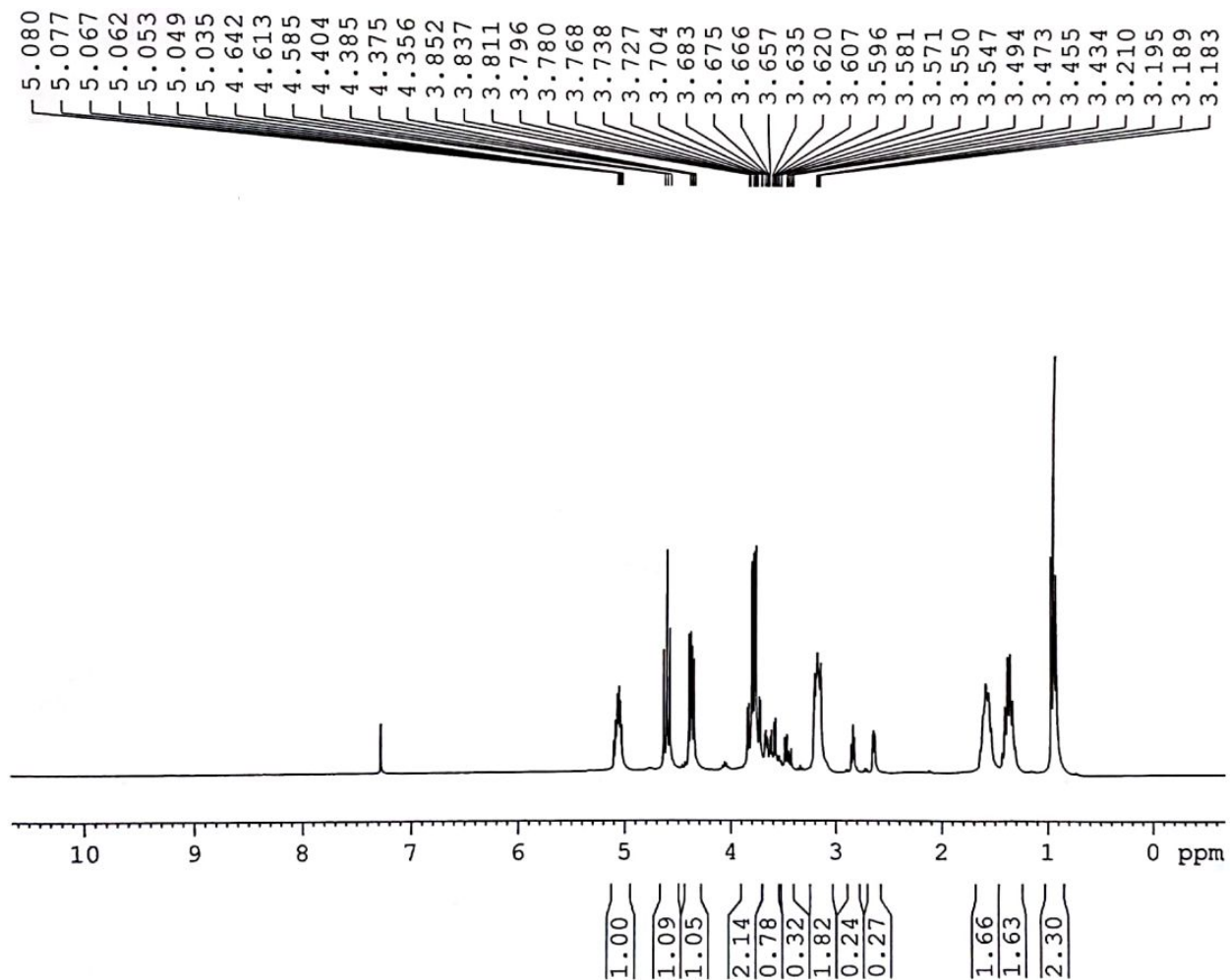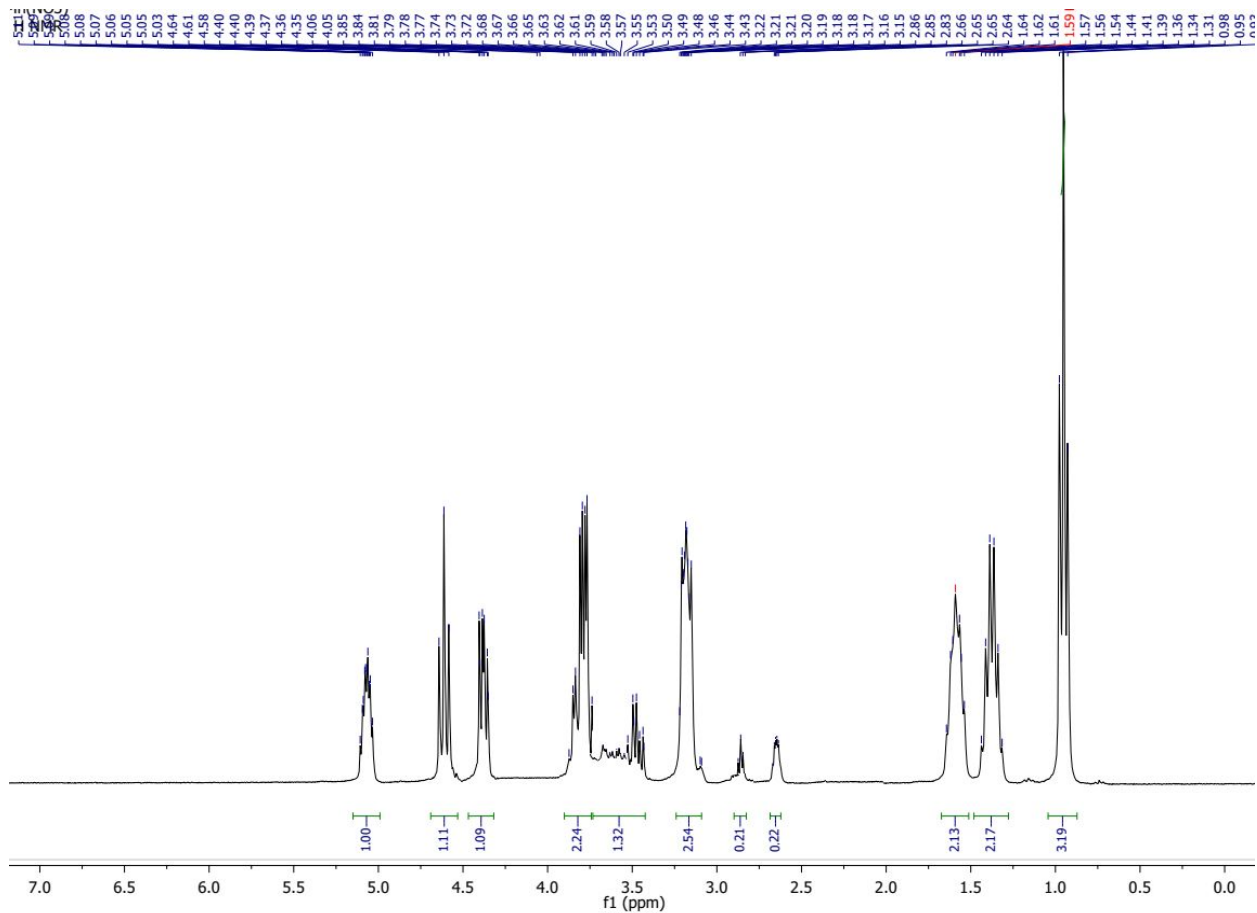
Figure S2. ^{1}H-NMR spectrum for data reported in Table 1, Entry 1.
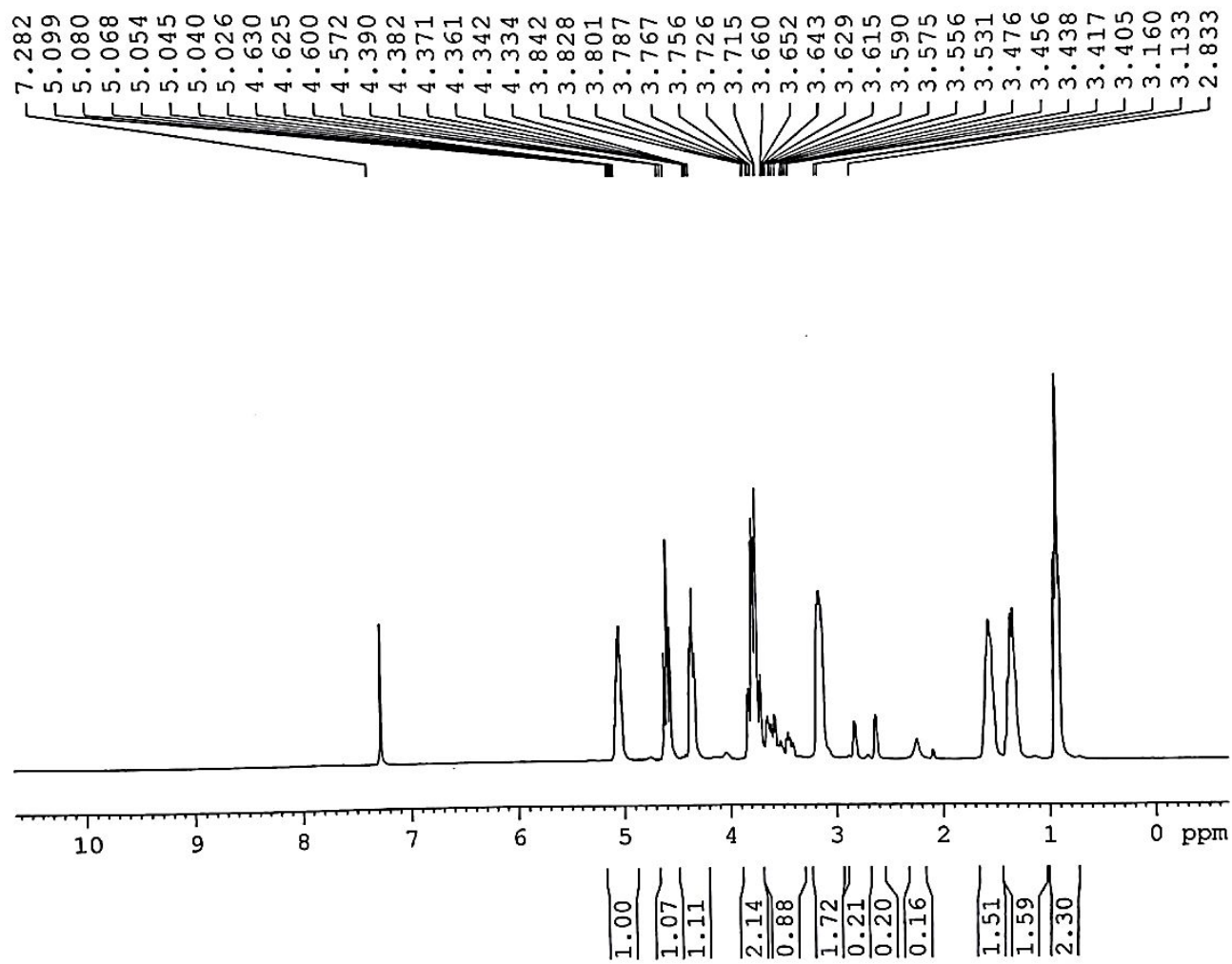
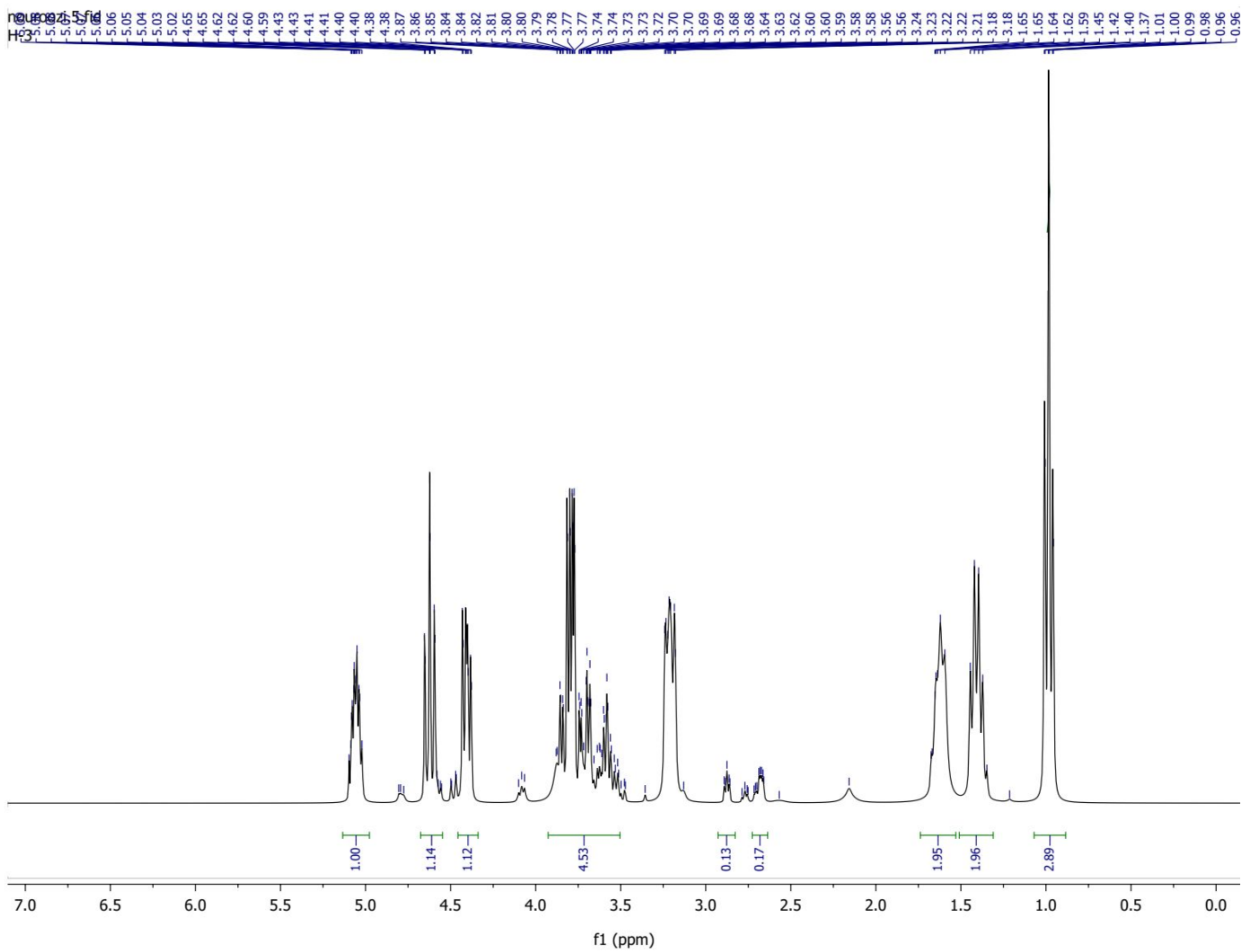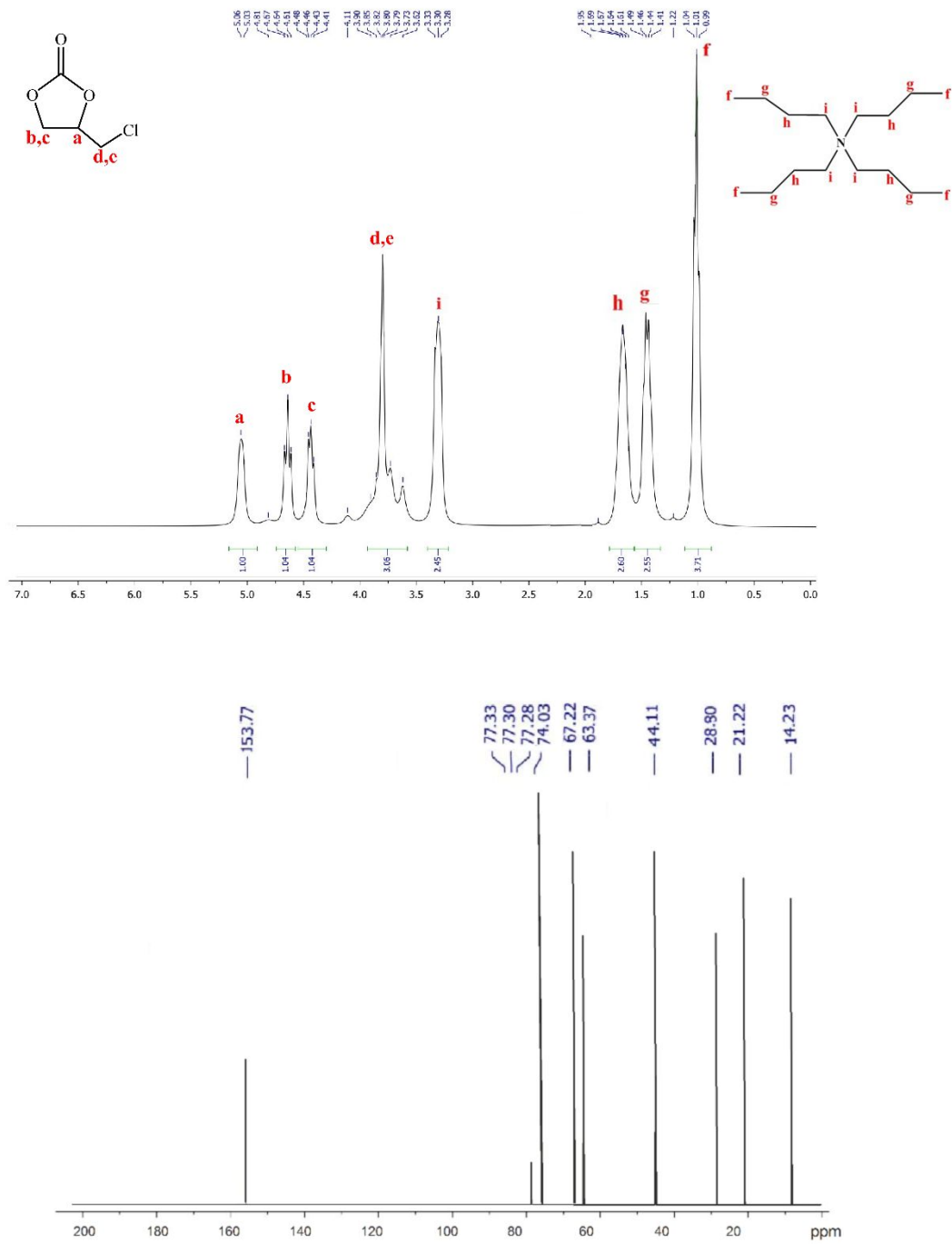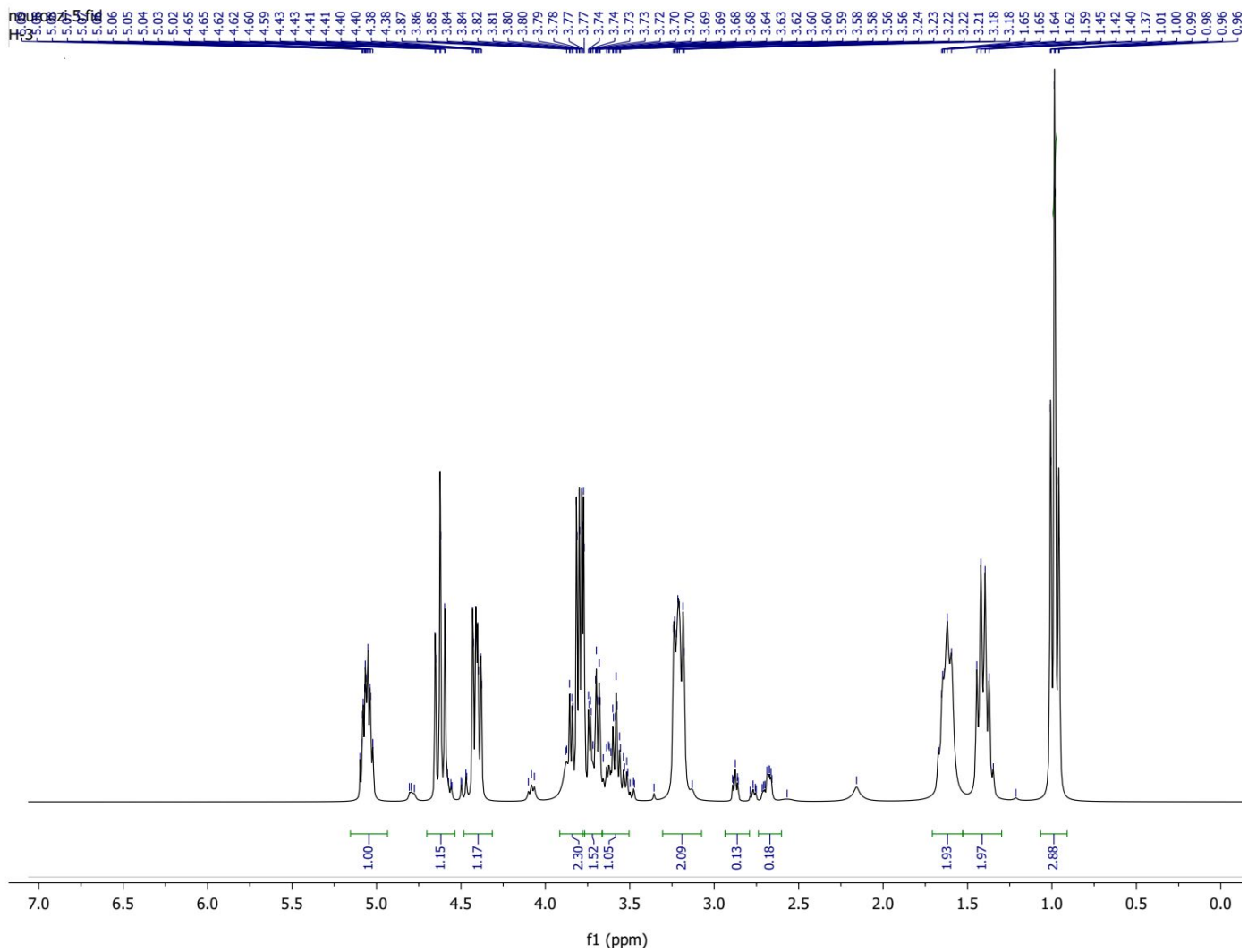**Figure S3.** ^{1}H-NMR spectrum for data reported in Table 1, Entry 2.

S8
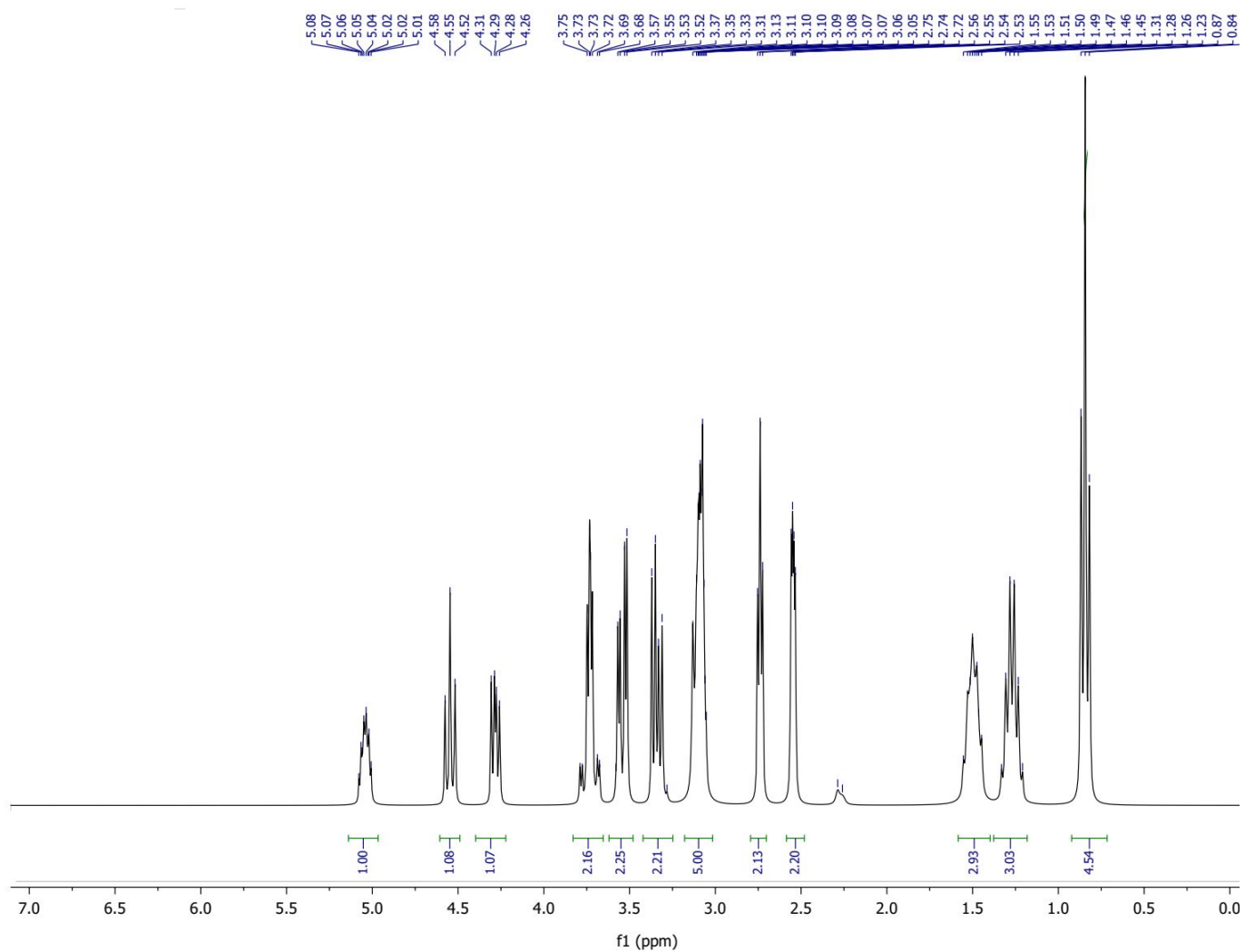
Figure S4. ^{1}H-NMR spectrum for data reported in Table 1, Entry 3.
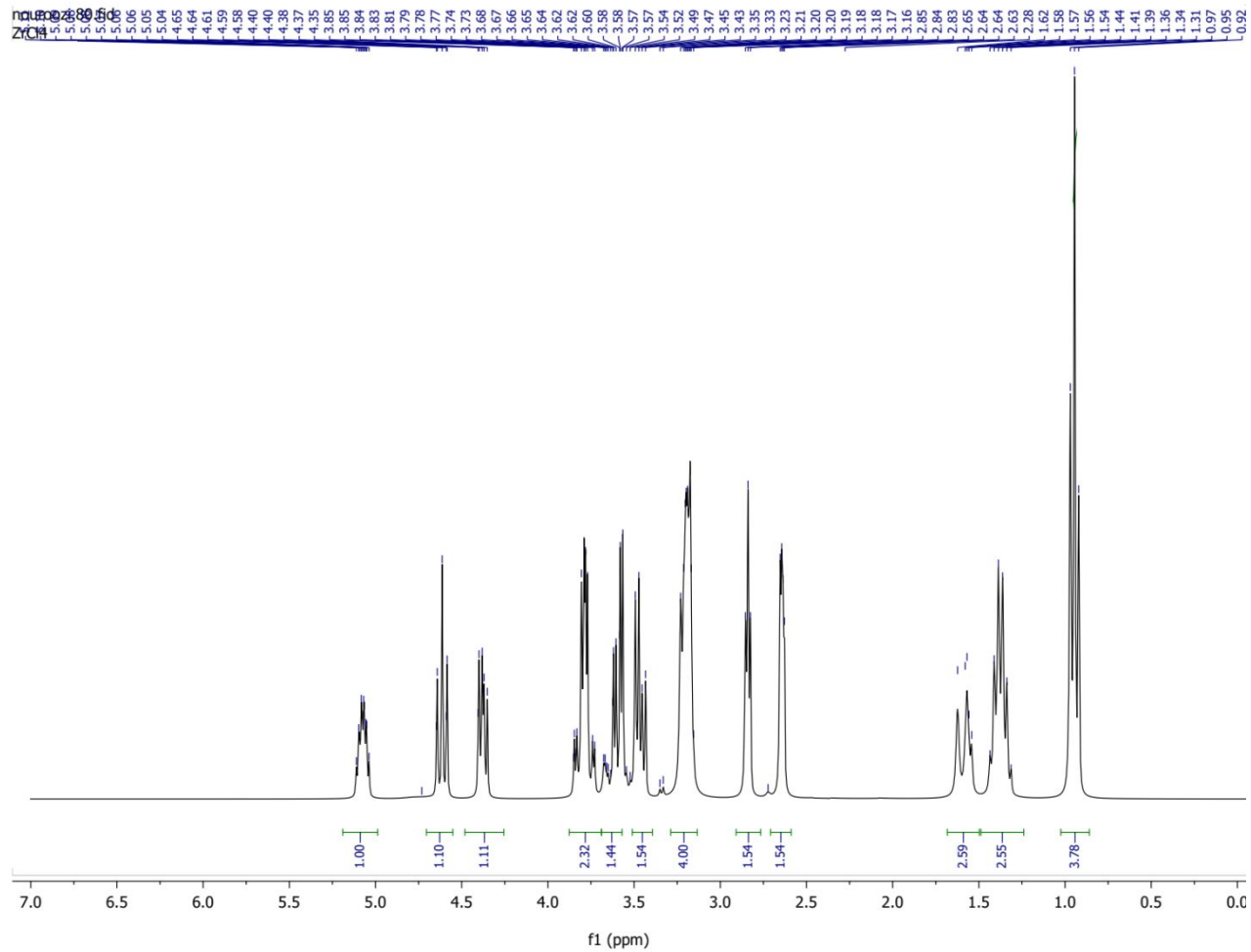
Figure S5. ^{1}H-NMR spectrum for data reported in Table 1, Entry 4.
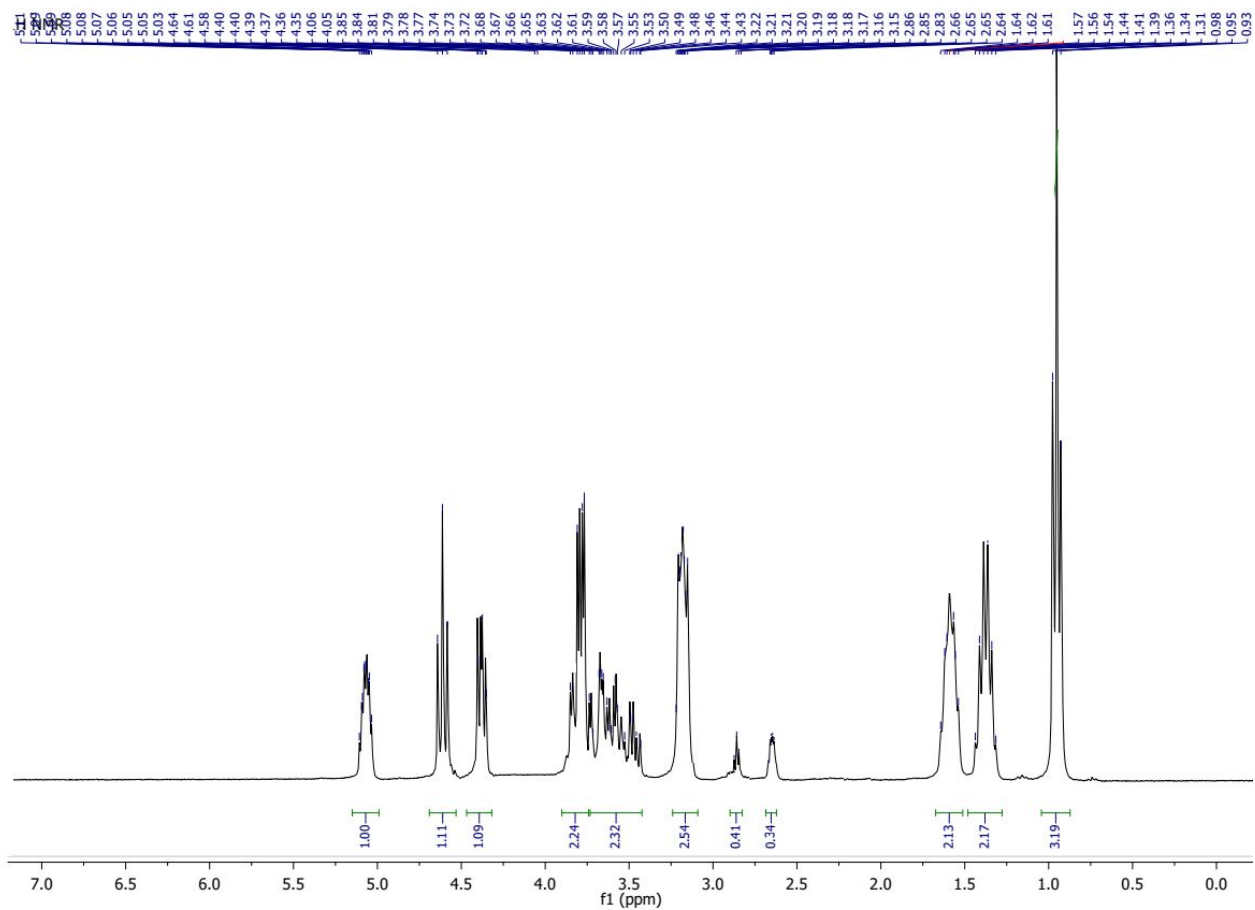
S10
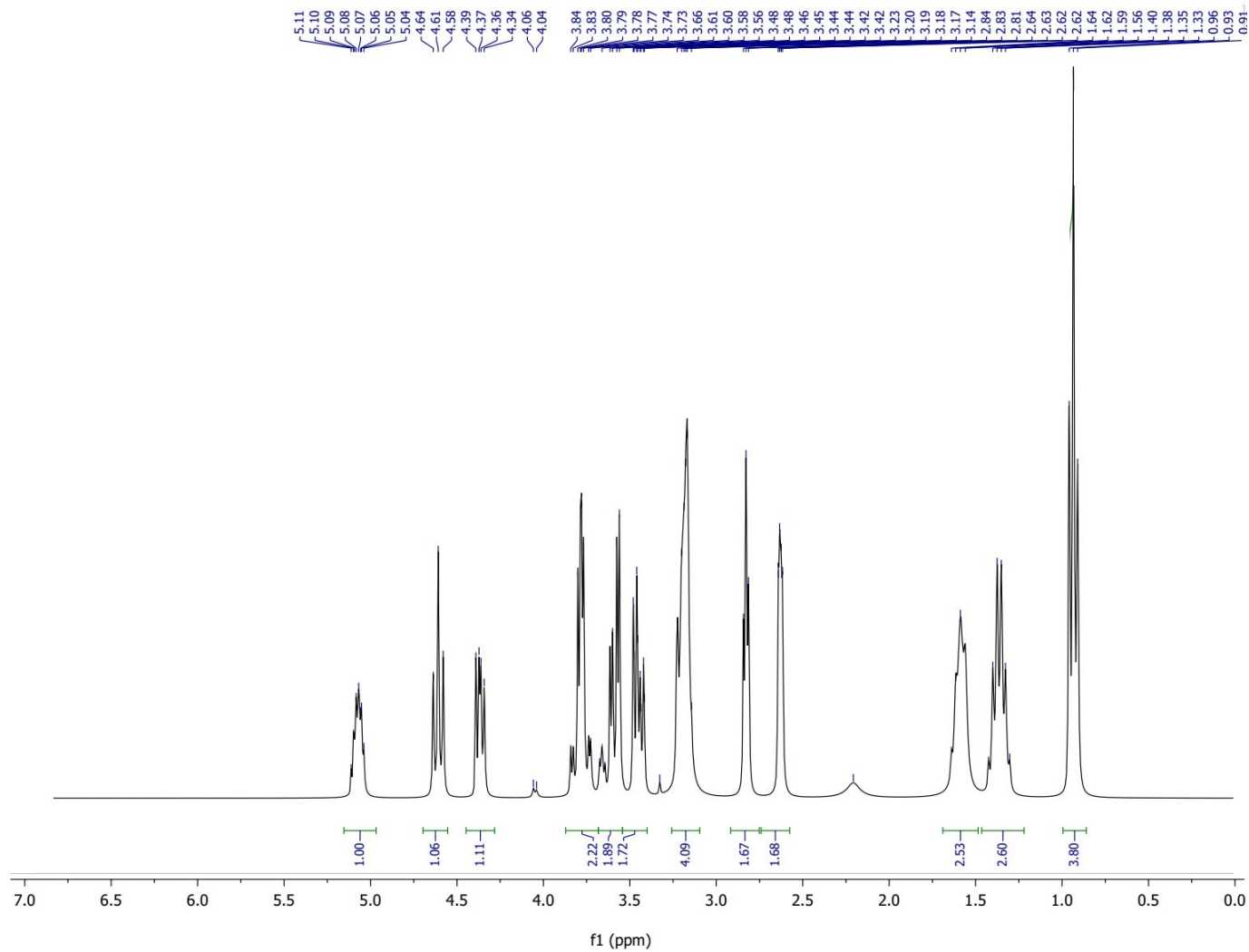
Figure S6. ^{1}H-NMR spectrum for data reported in Table 1, Entry 5.
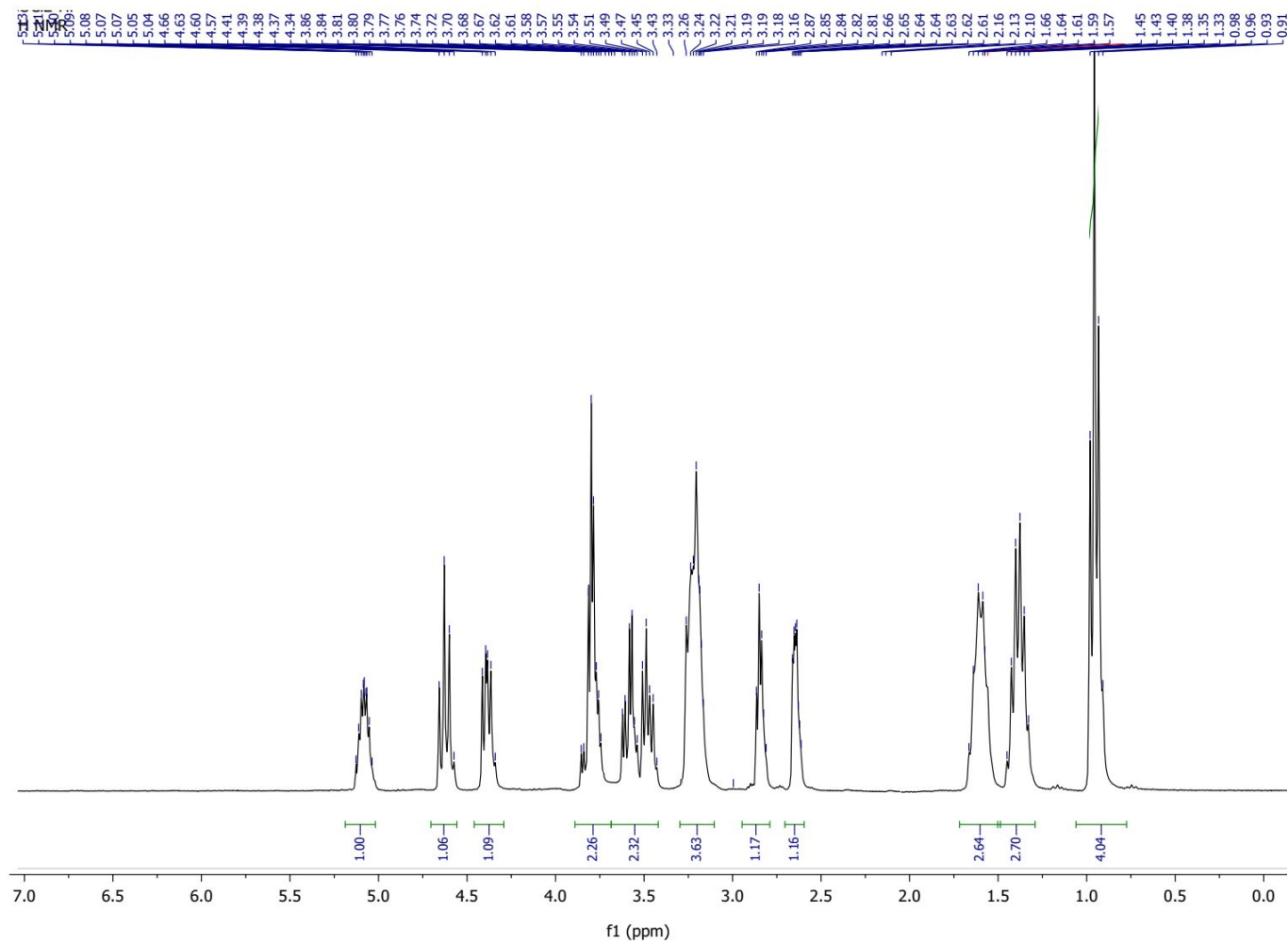
Figure S7. ^{1}H-NMR spectrum for data reported in Table 1, Entry 6.
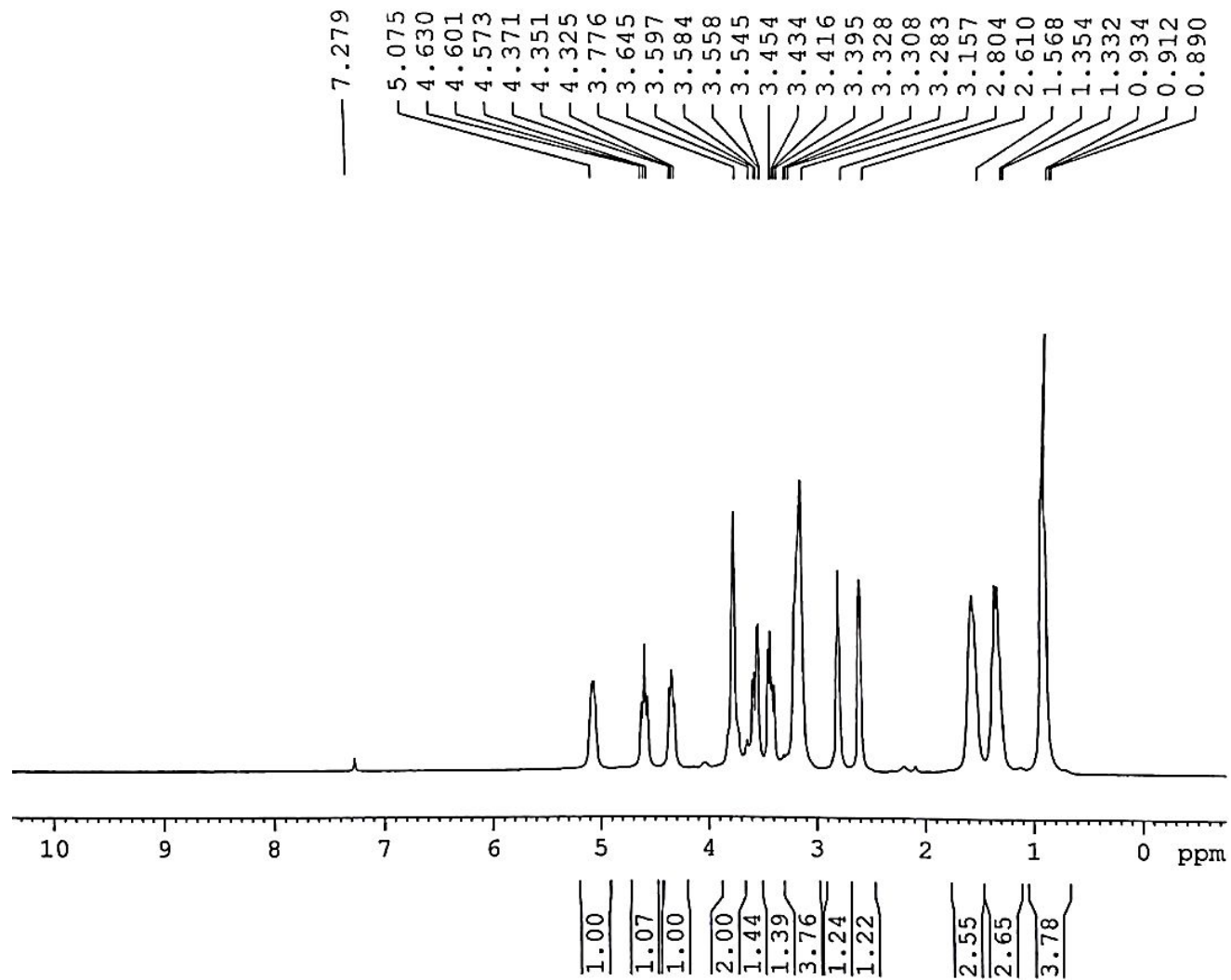
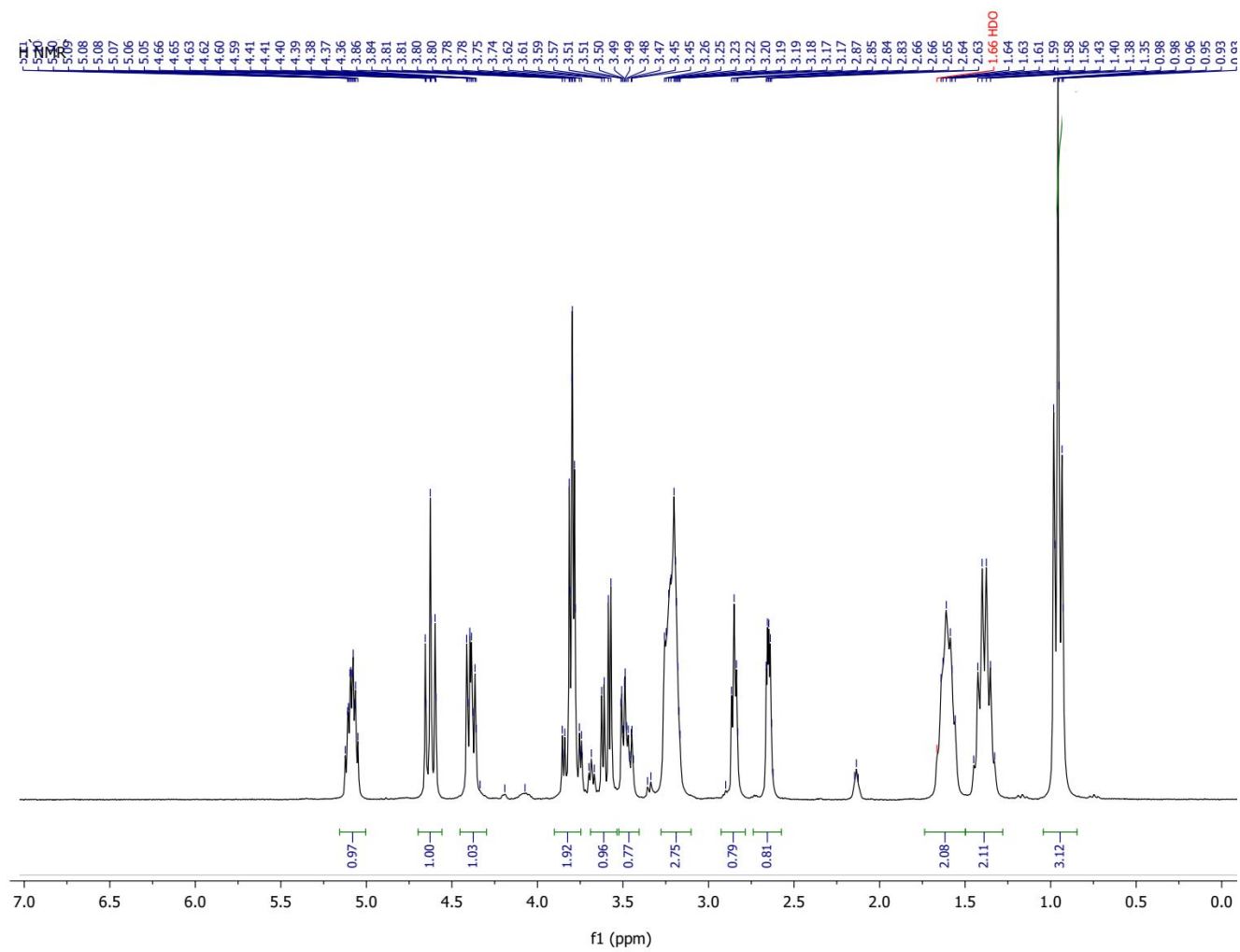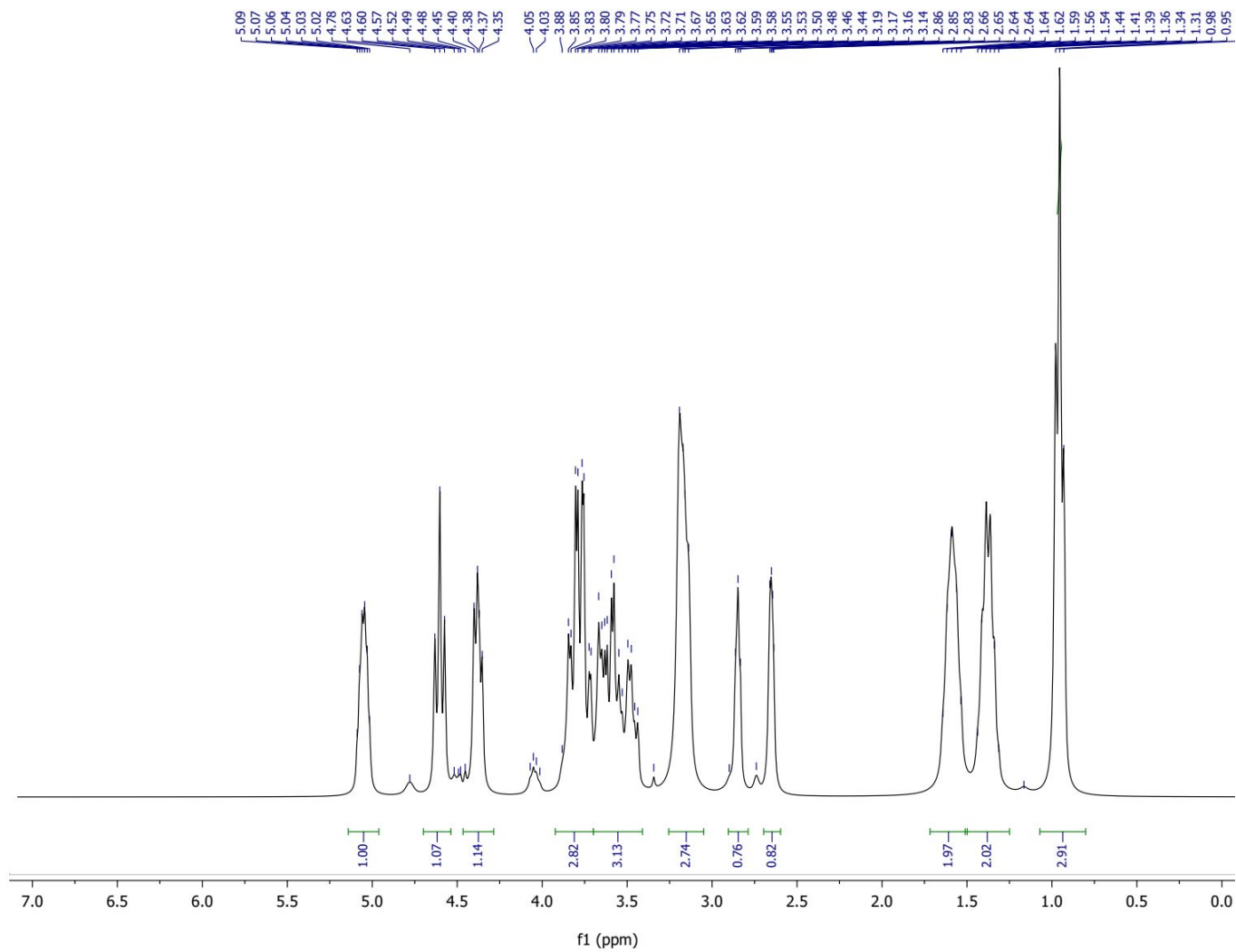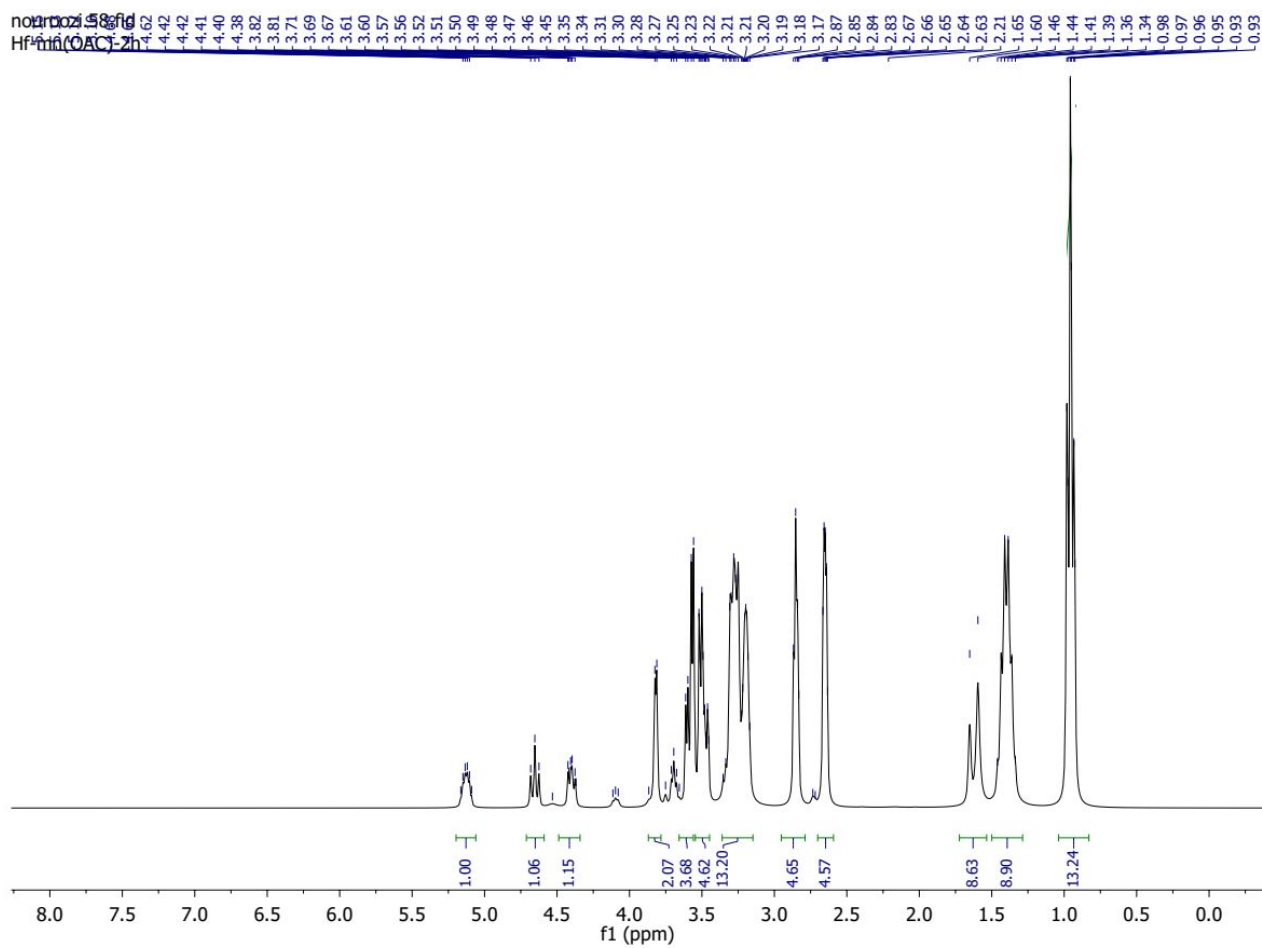**Figure S8.** ^{1}H-NMR spectrum for data reported in Table 1, Entry 7.

S13
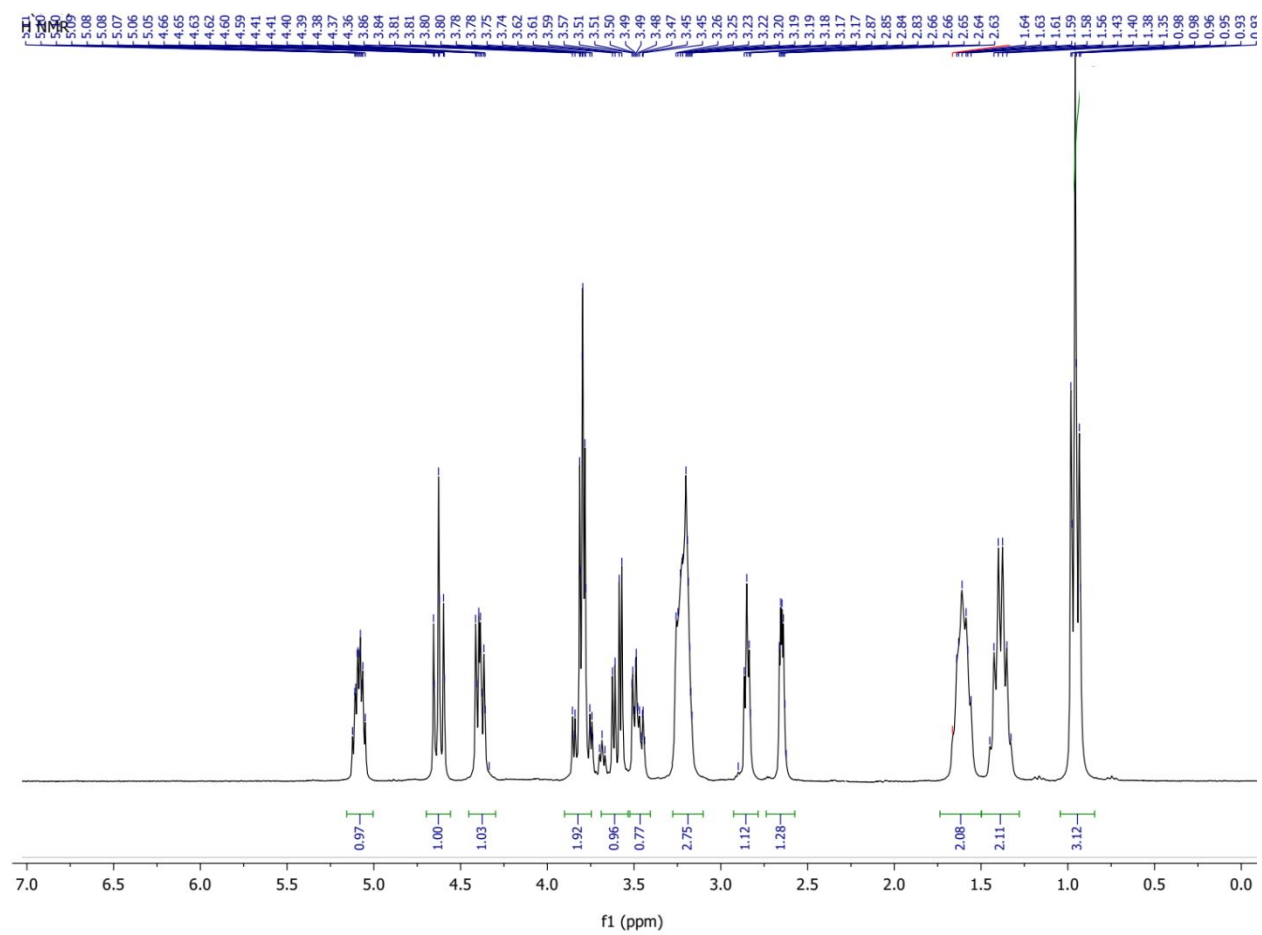
Figure S9. ^{1}H-NMR spectrum for data reported in Table 1, Entry 8.
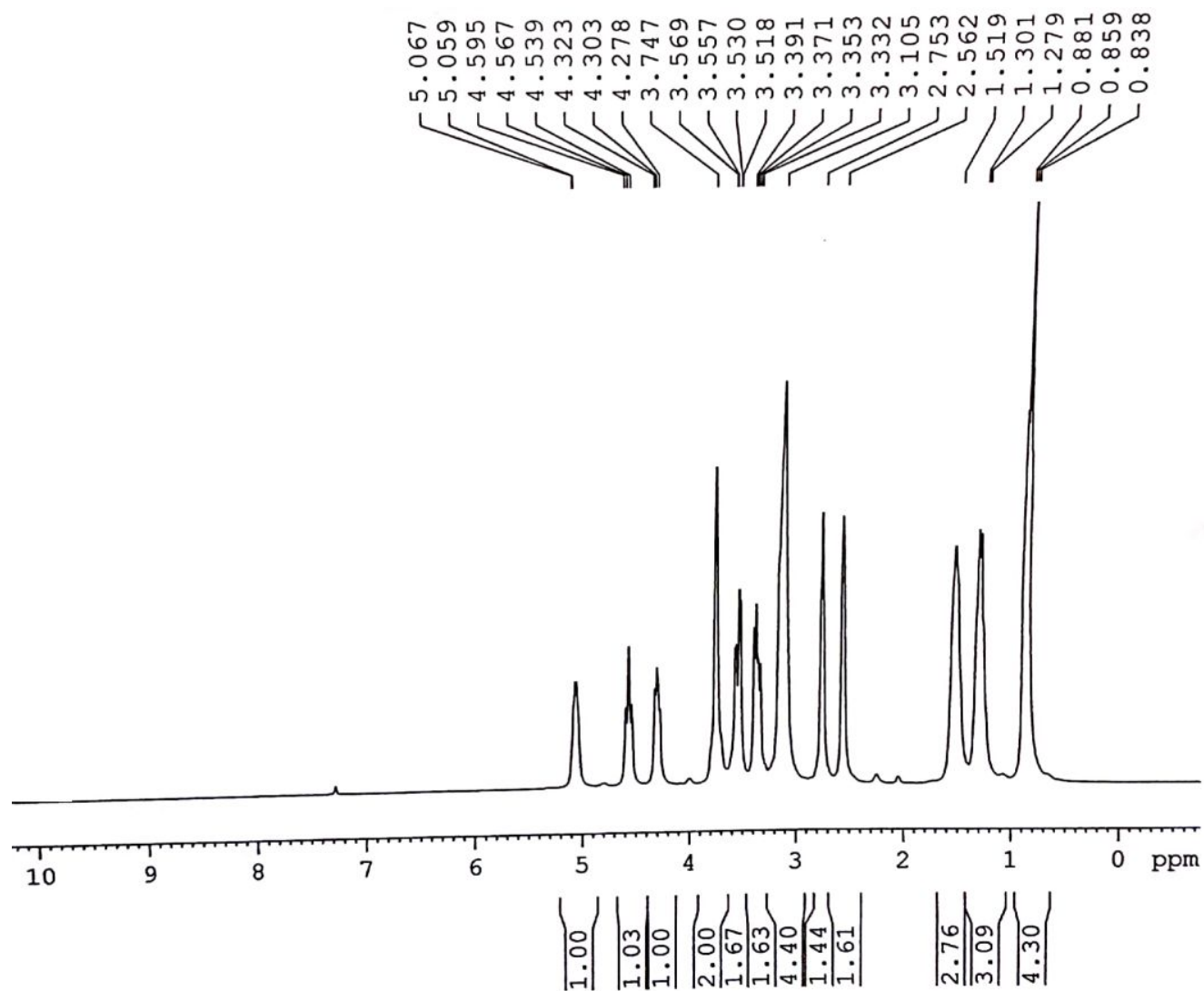
Figure S10. ^{1}H-NMR spectrum for data reported in Table 1, Entry 9.

S15
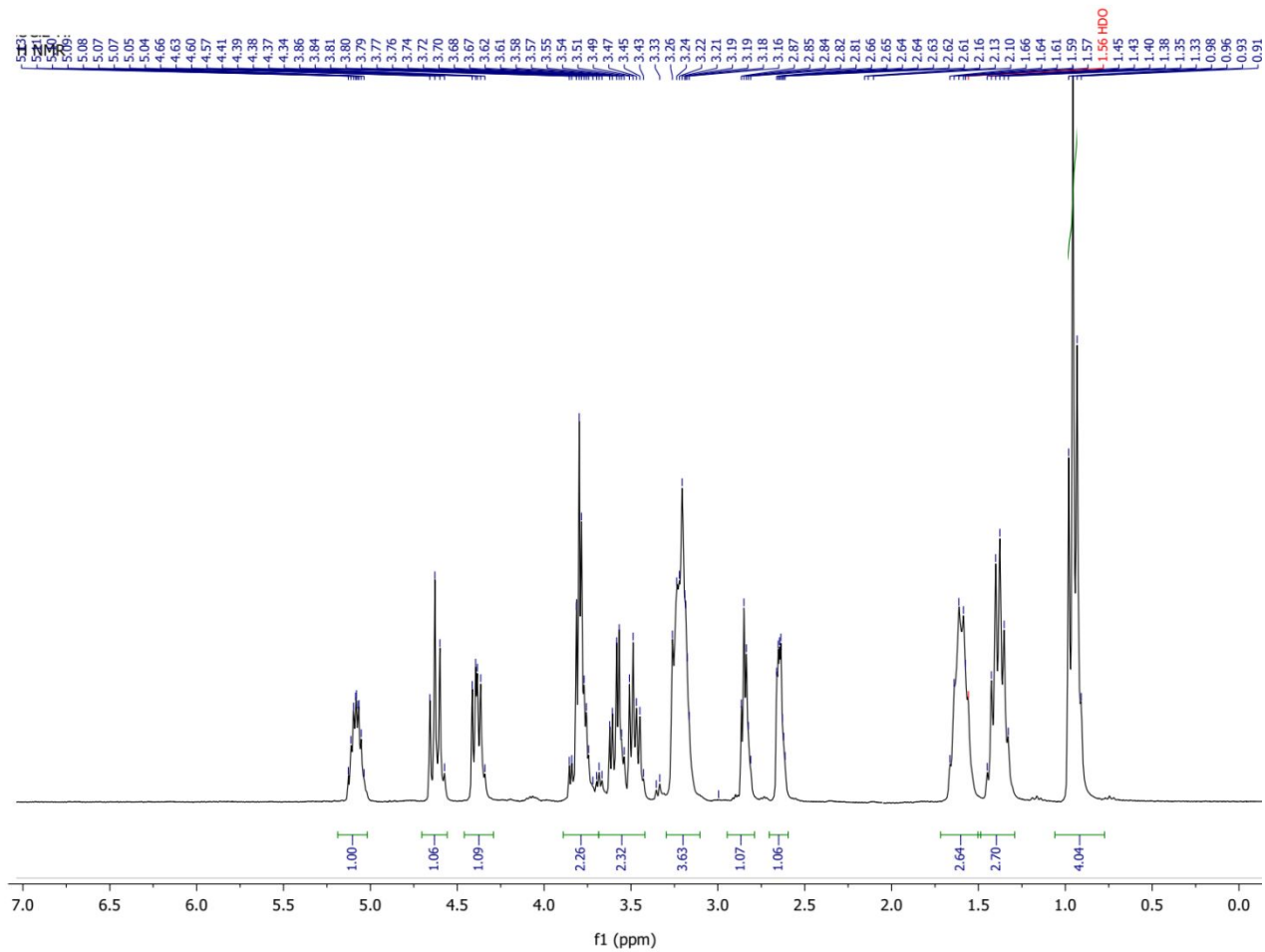
Figure S11. ^{1}H-NMR spectrum for data reported in Table 1, Entry 10.

S16
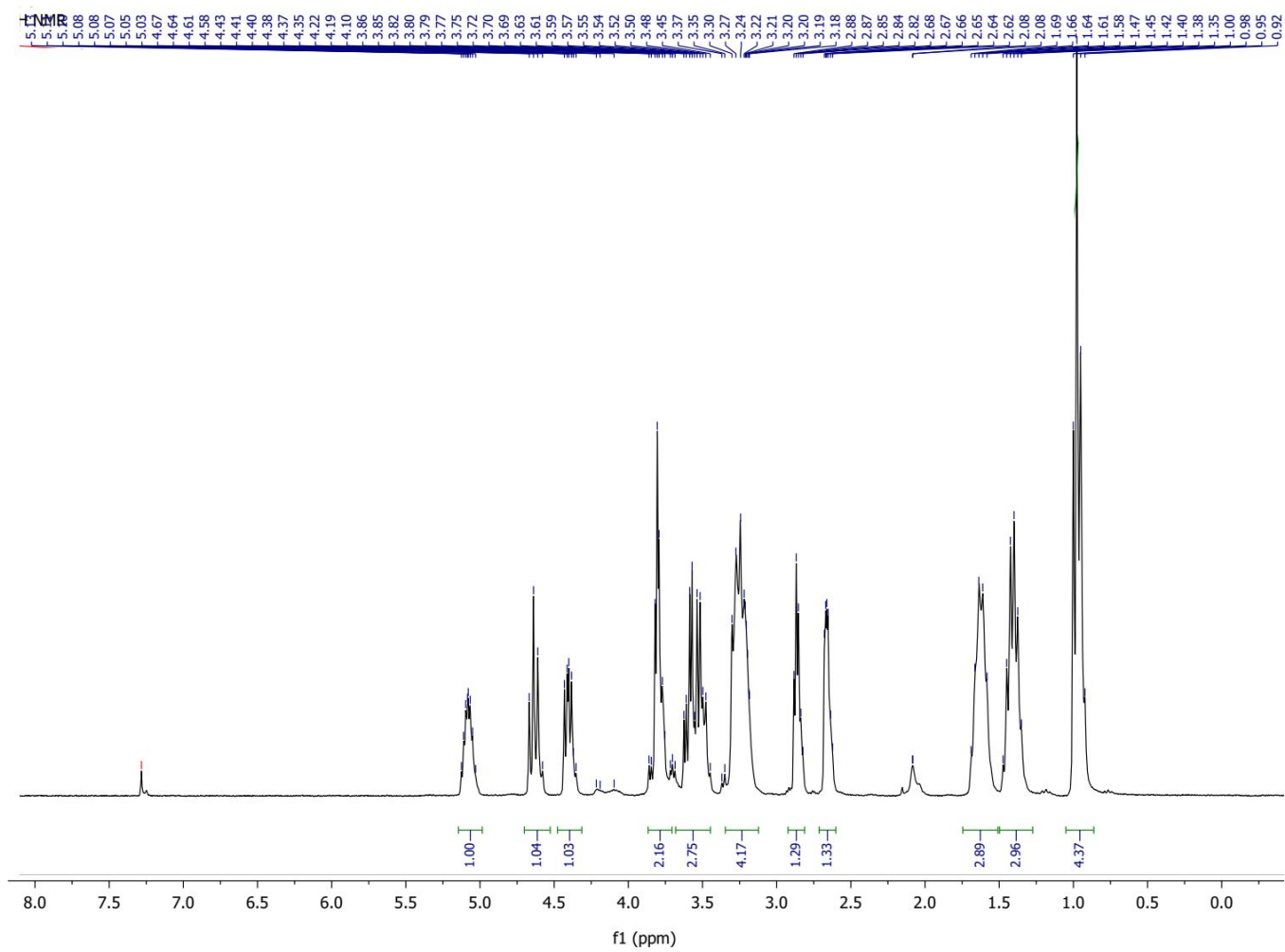
Figure S12. ^{1}H-NMR spectrum for data reported in Table 1, Entry 11.
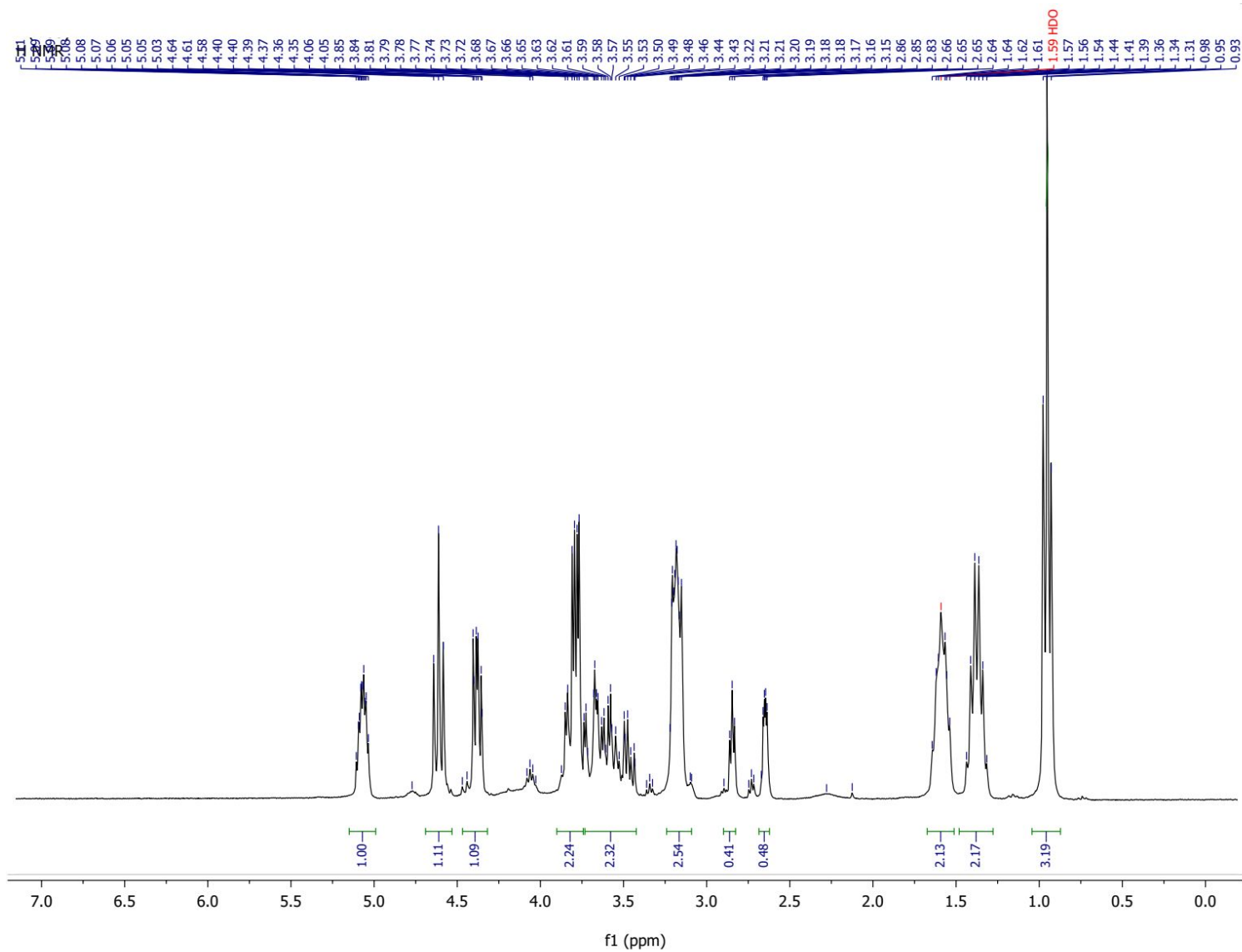
Figure S13. ^{1}H-NMR spectrum for data reported in Table 1, Entry 12.
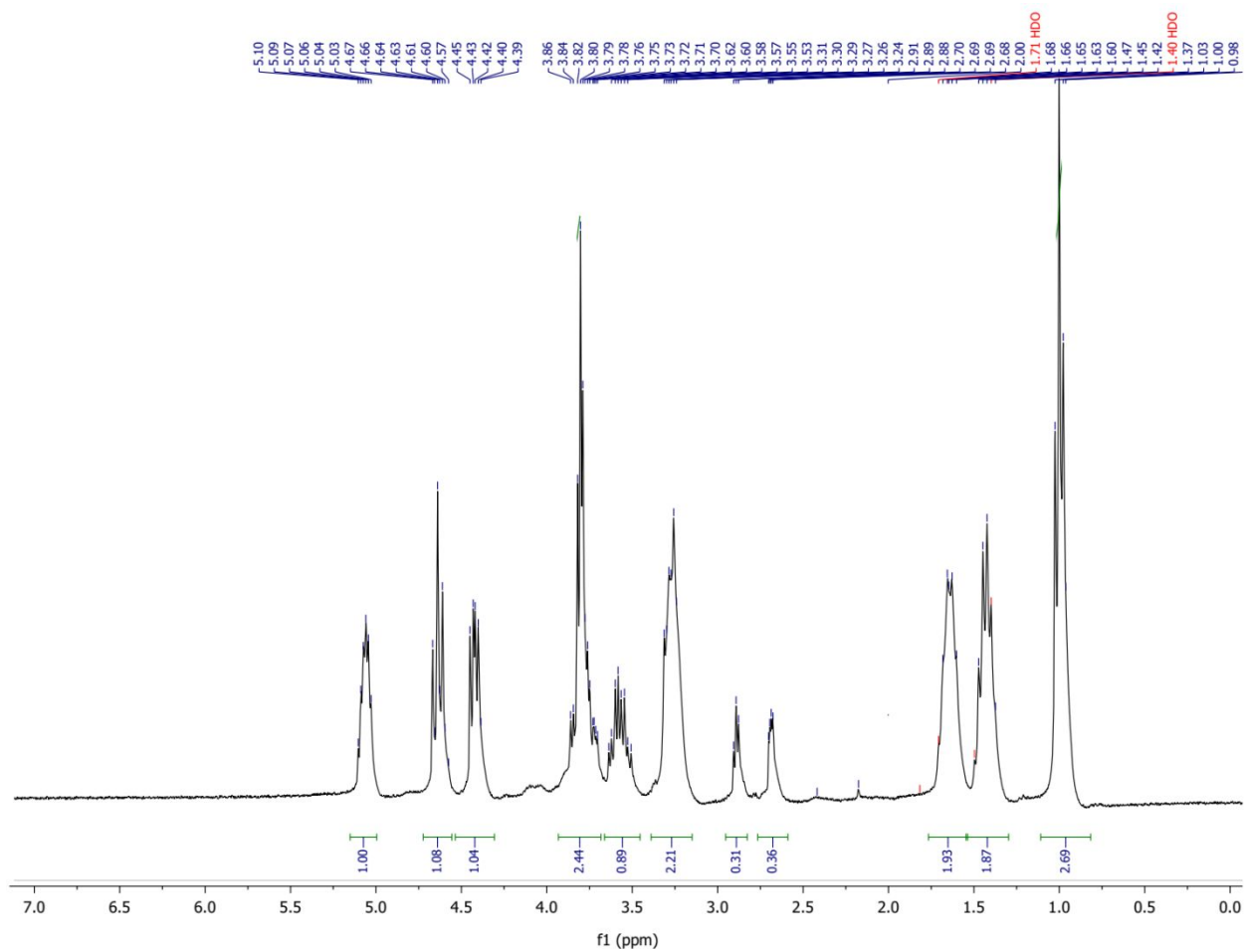
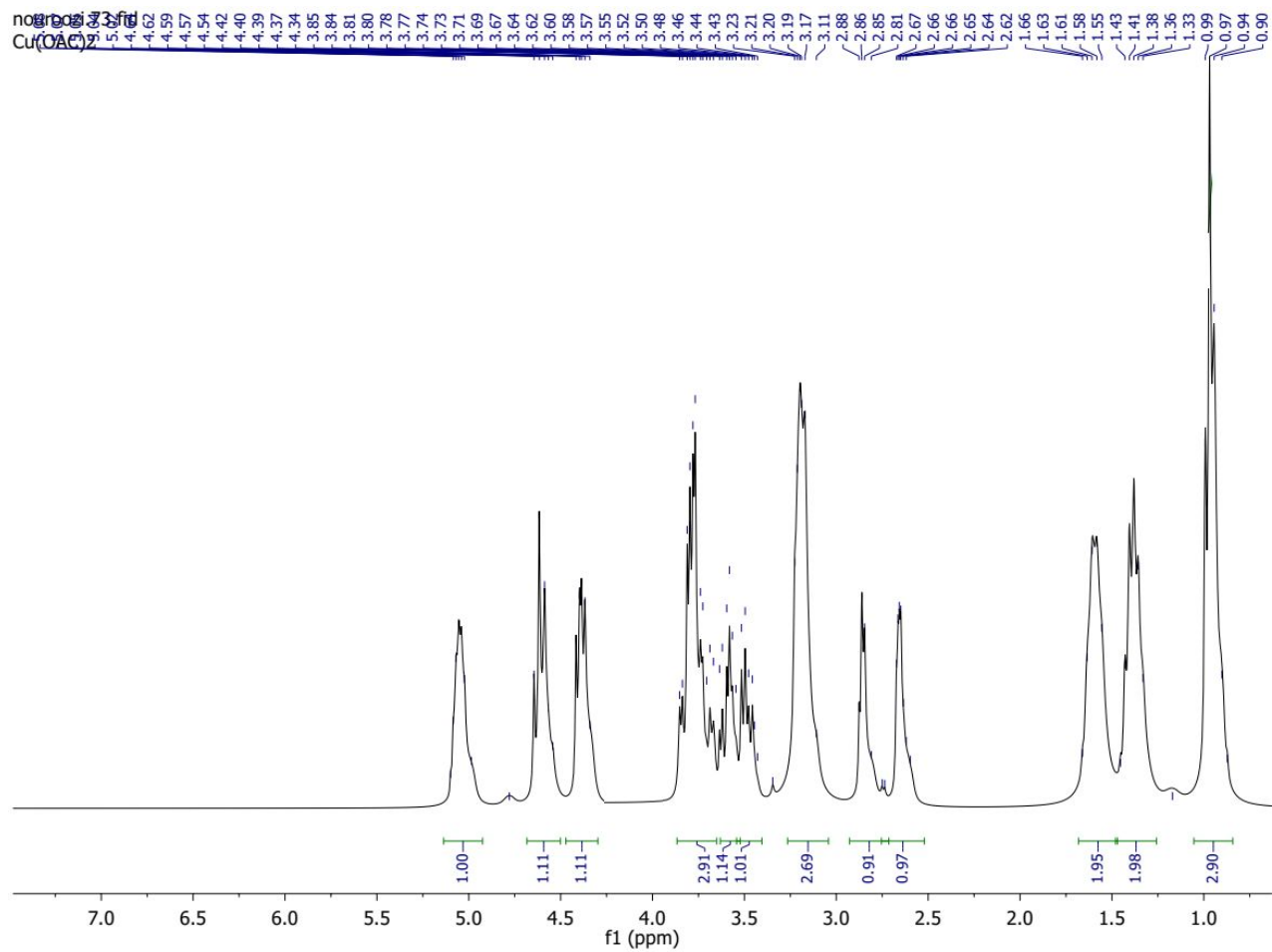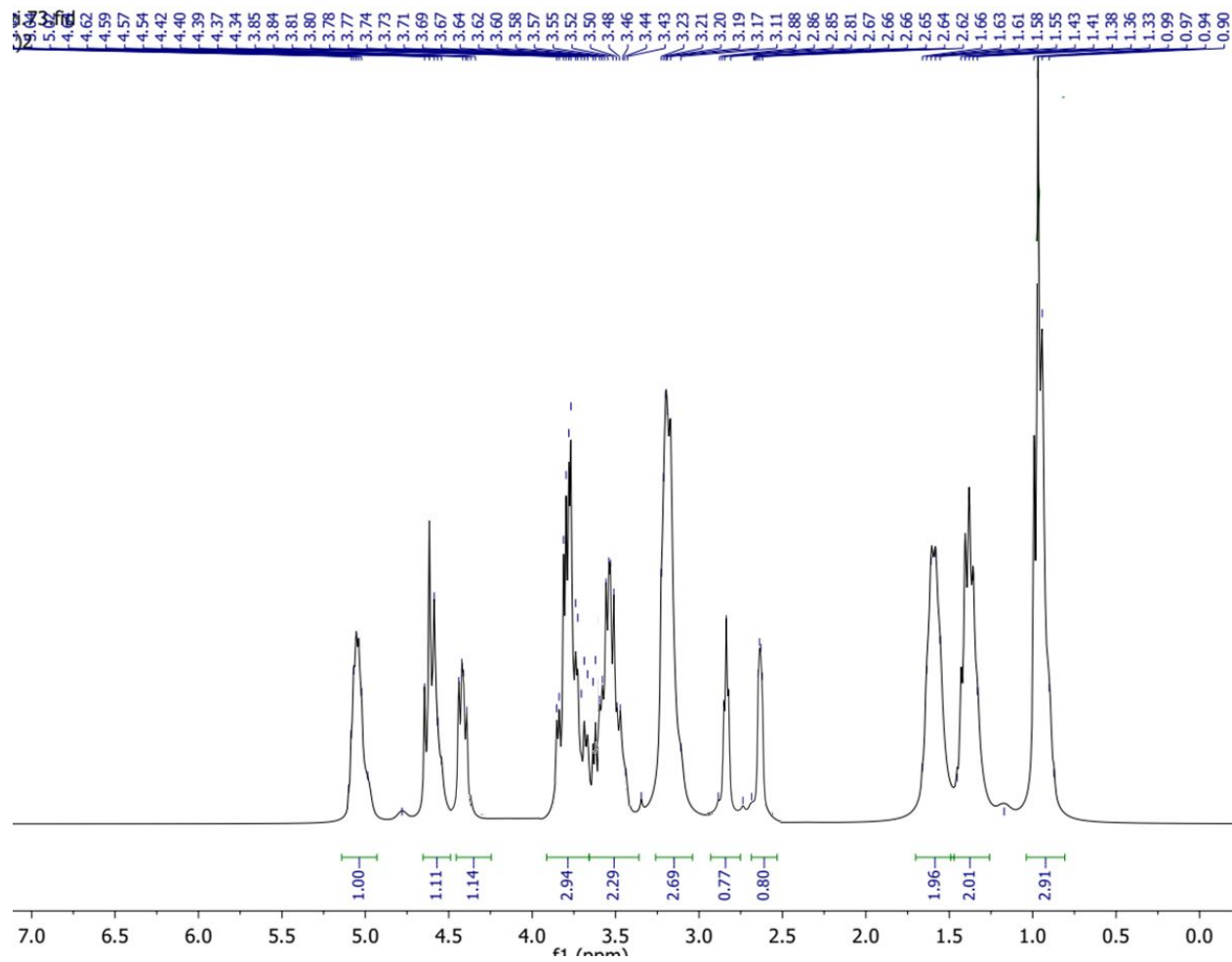**Figure S14.** ^{1}H-NMR spectrum for data reported in Table 1, Entry 13.

S19
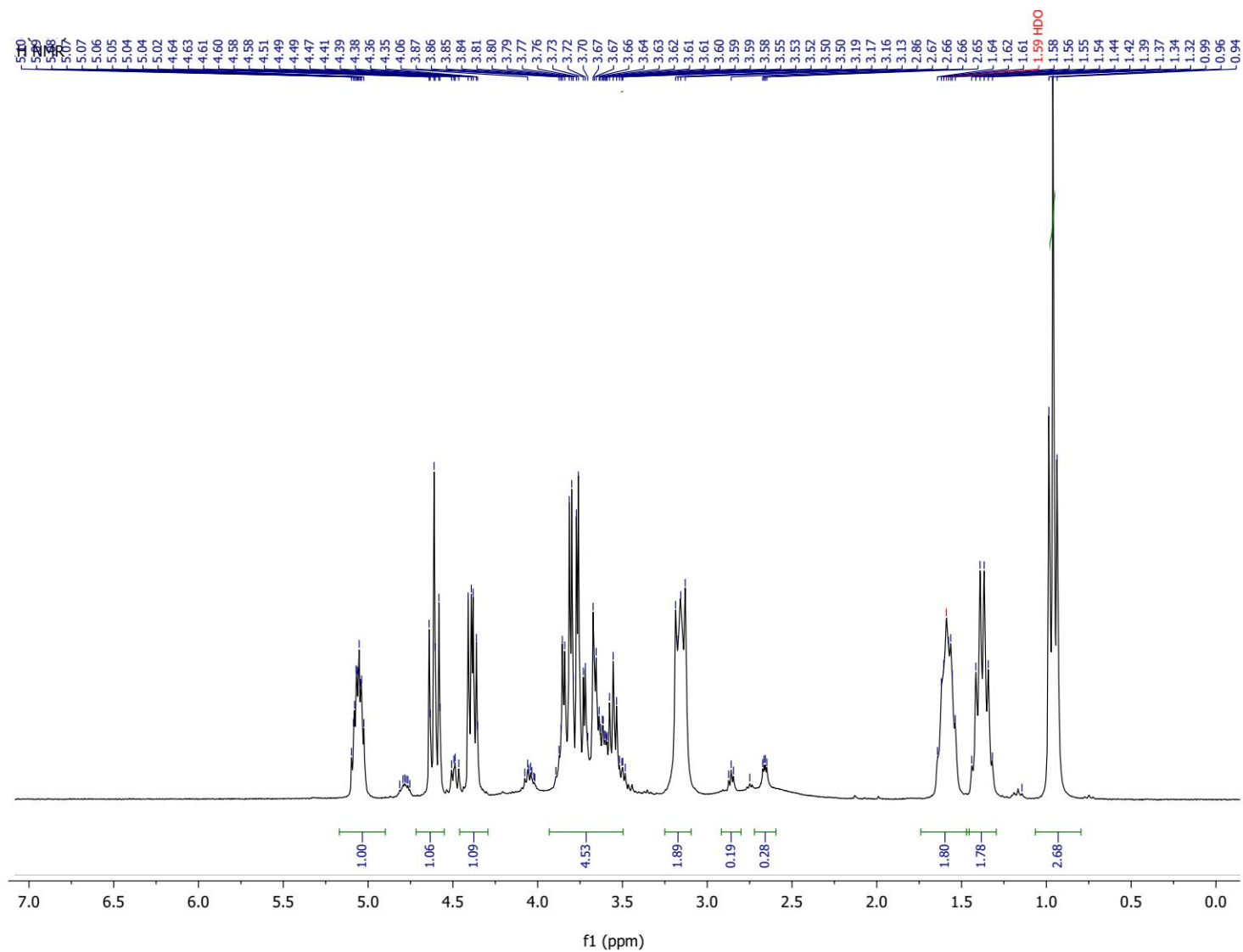
Figure S15. ¹H-NMR spectrum for data reported in Table 1, Entry 14.
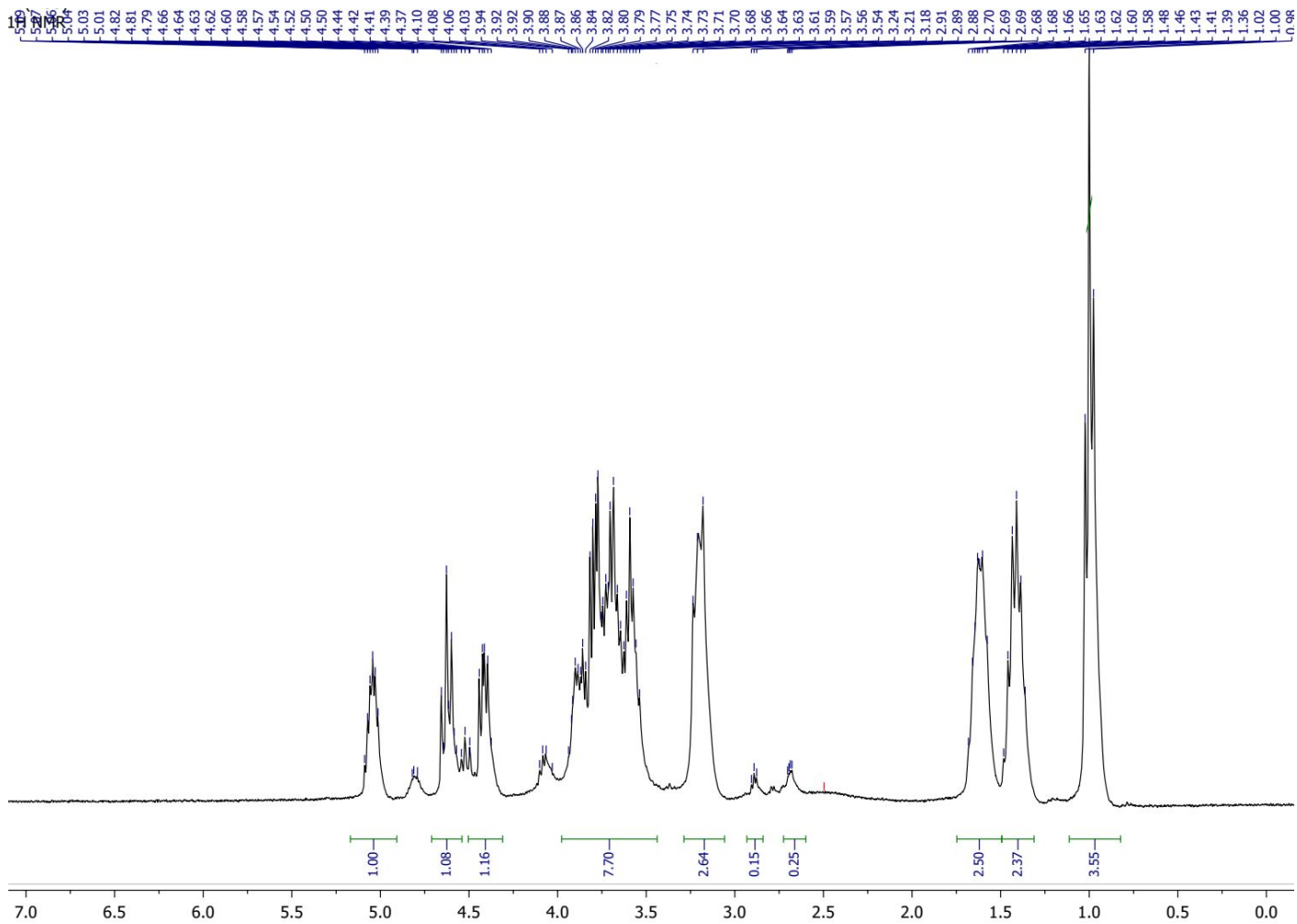
Figure S16. ^{1}H-NMR spectrum for data reported in Table 1, Entry 15.

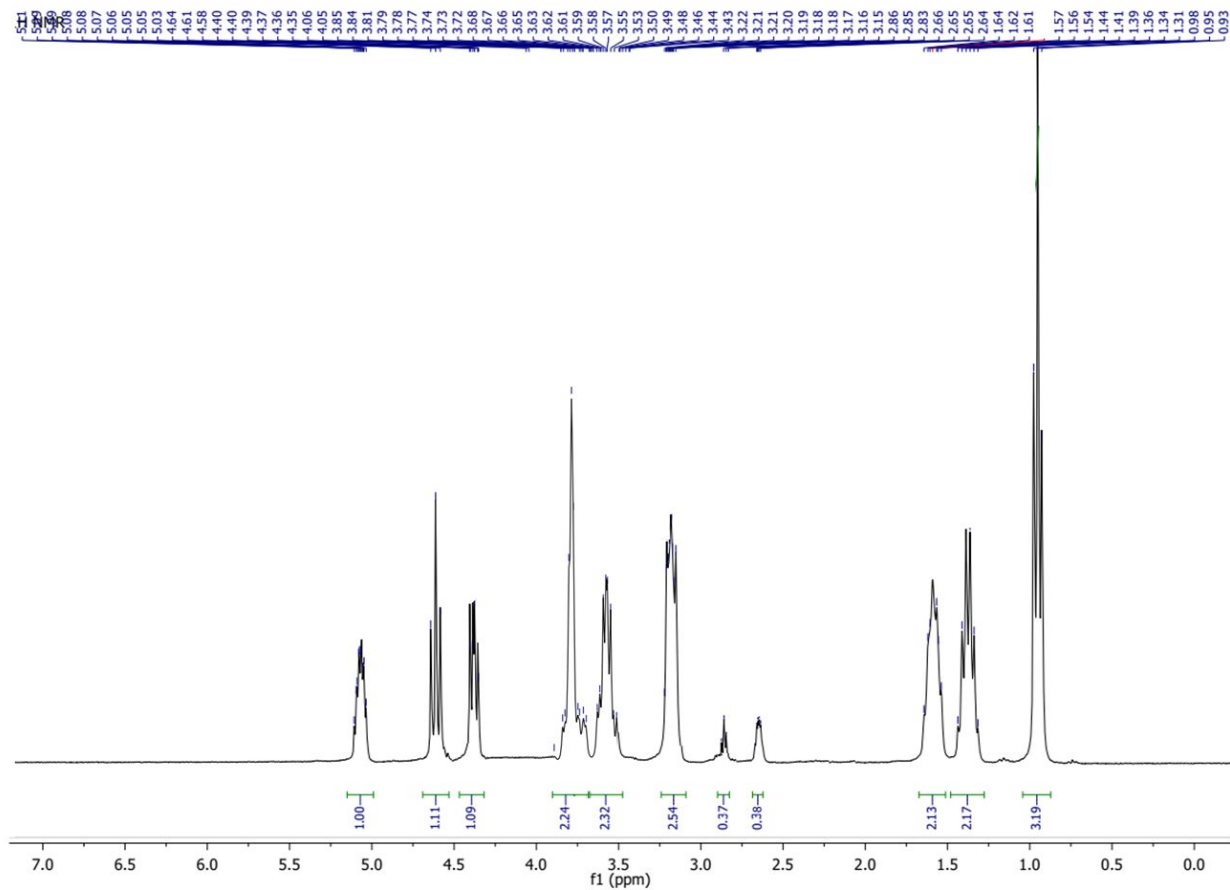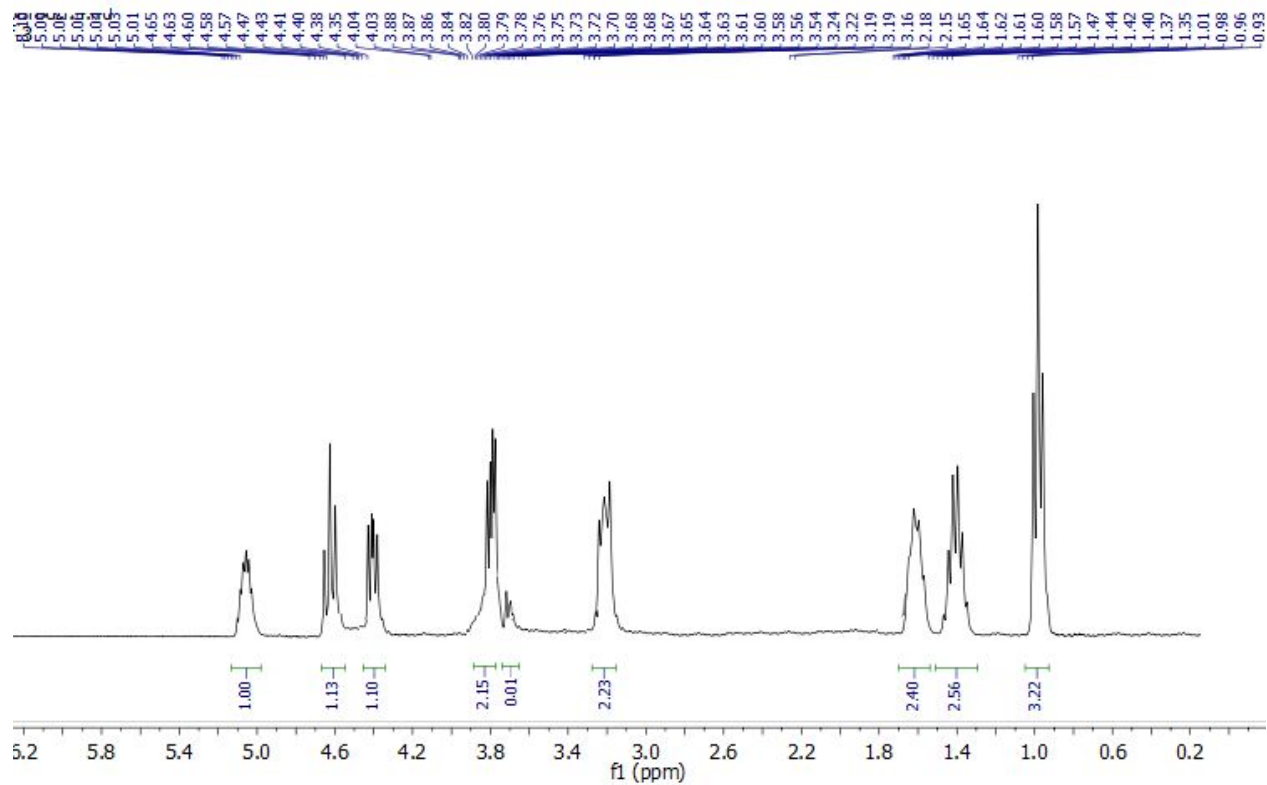**Figure S17.** ¹H-NMR spectrum for data reported in Table 1, Entry 16.

Figure S18. ^{1}H-NMR spectrum for data reported in Table 1, Entry 17.

Figure S19. ^{1}H-NMR and ^{13}C-NMR spectrum for data reported in Table 1, Entry 18.
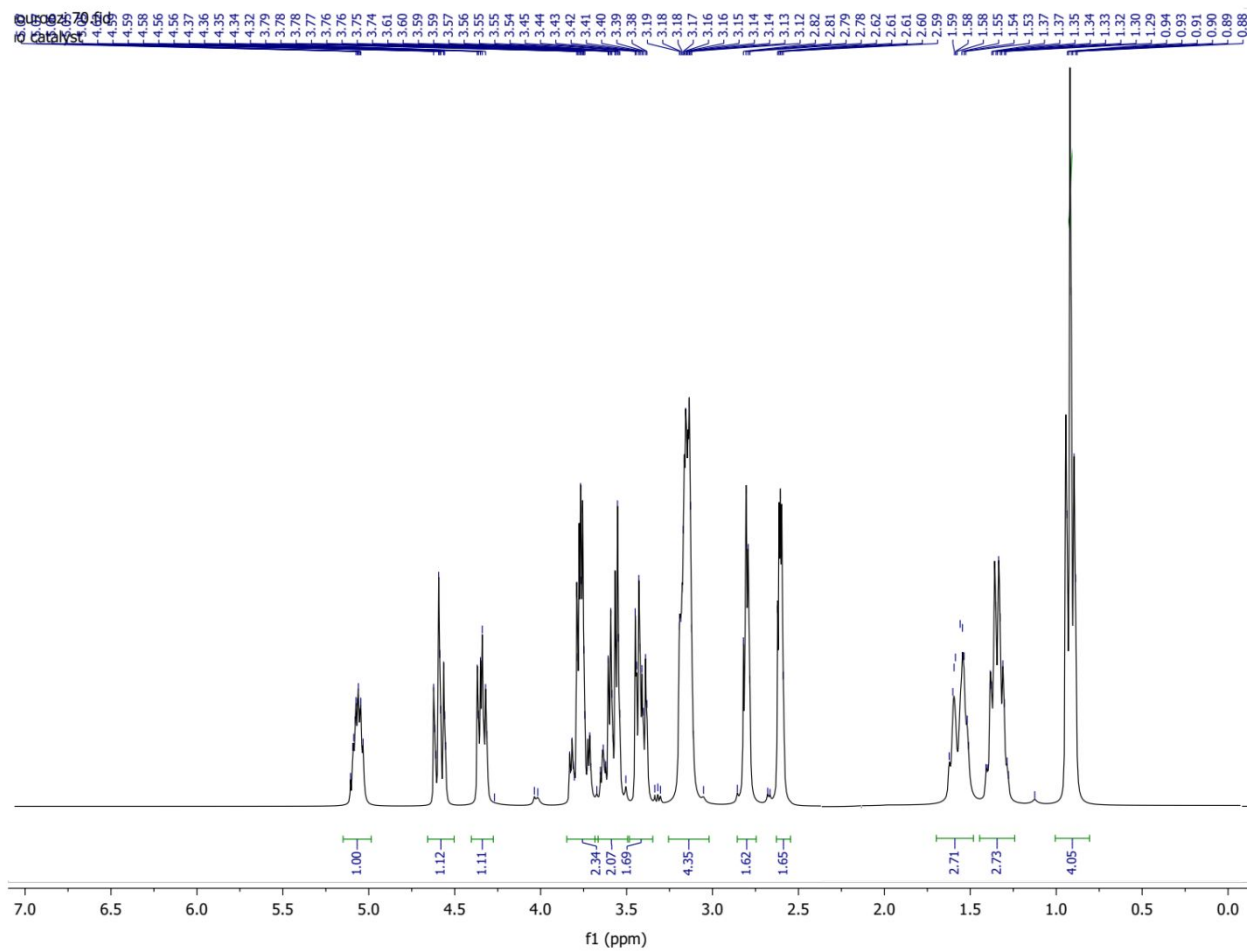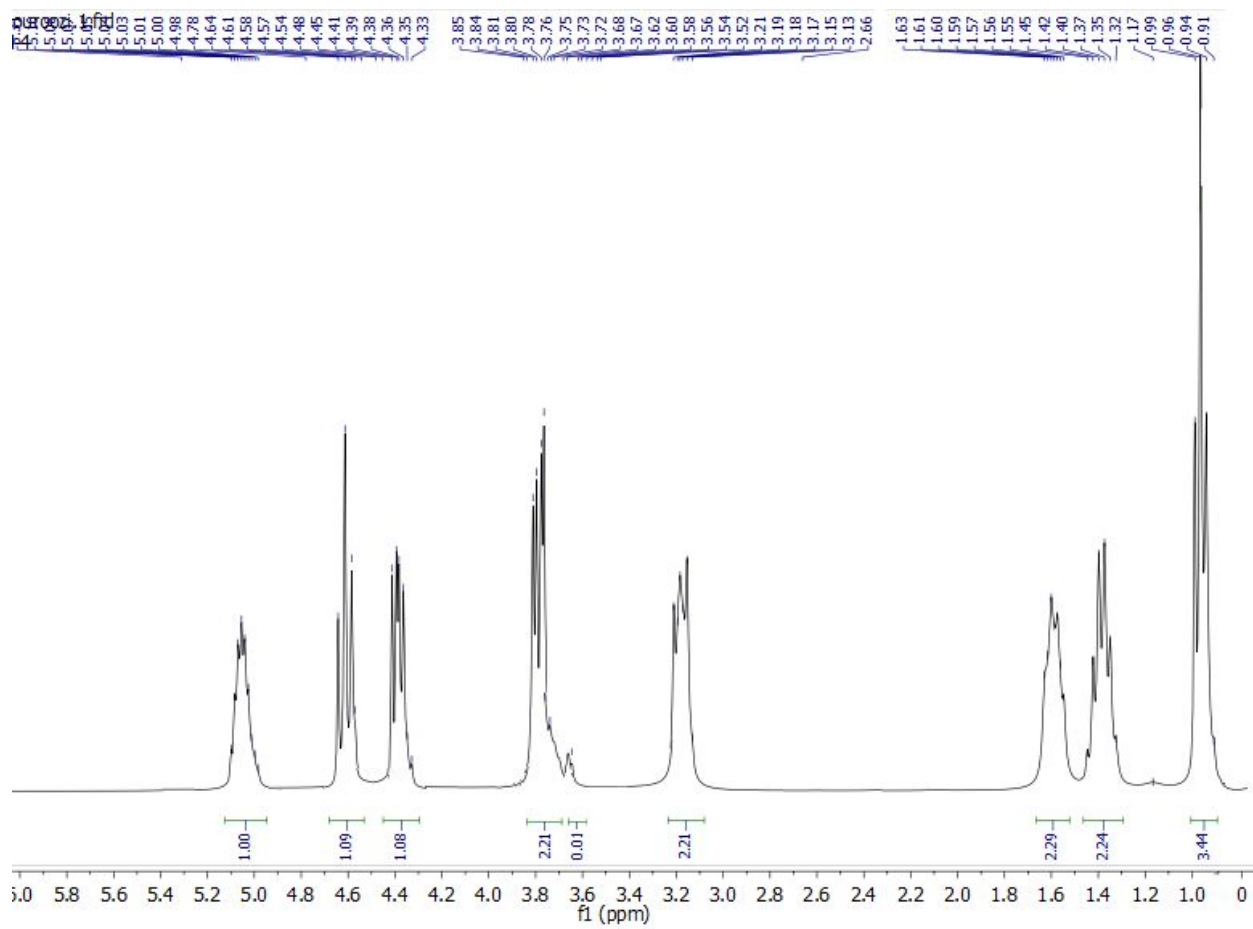
Figure S20. ^{1}H-NMR spectrum for data reported in Table 1, Entry 19.

Figure S21. ^{1}H-NMR spectrum for data reported in Table 1, Entry 20.
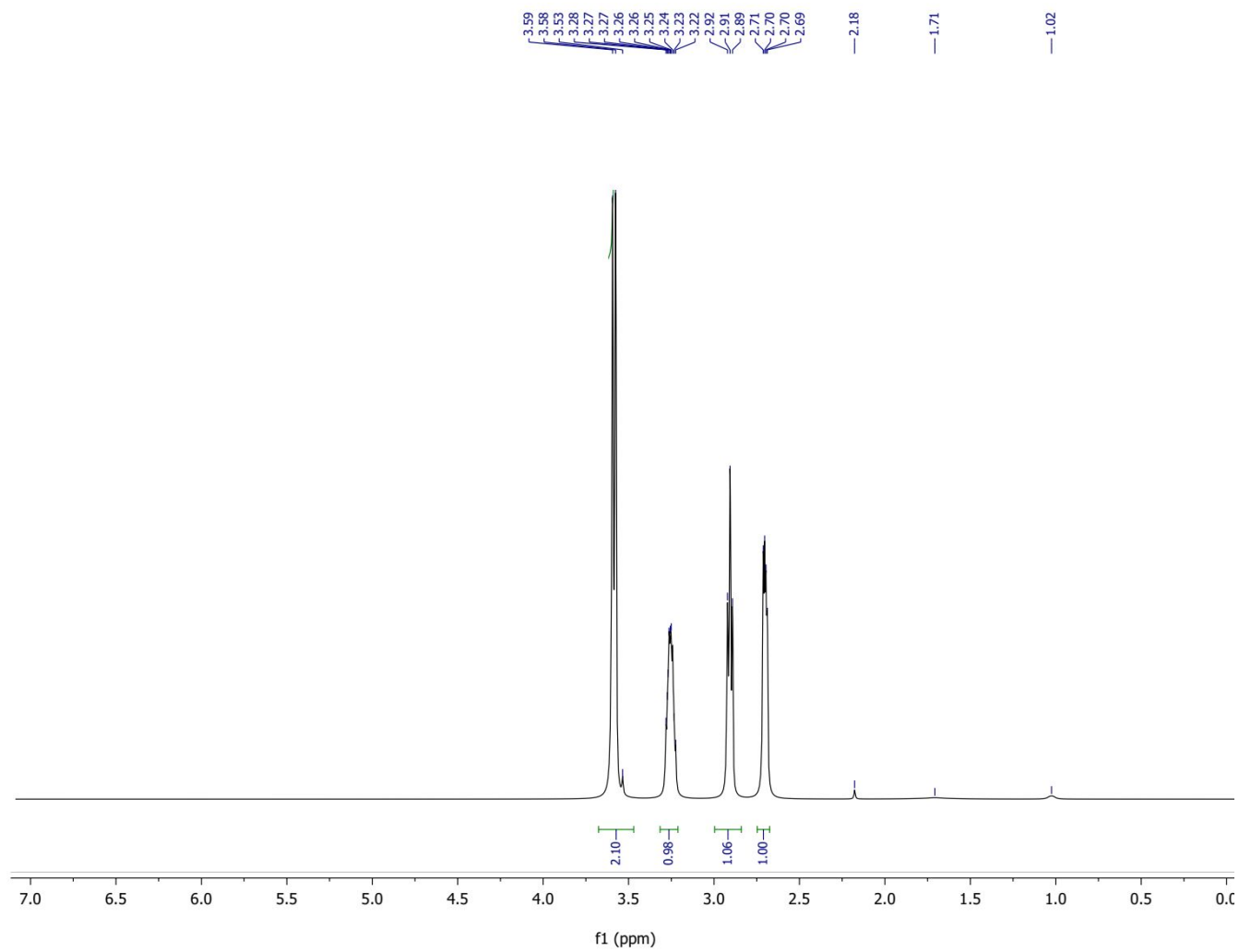
S26

Figure S22. NMR spectrum for data reported in Table 1, Entry 21.

Figure S23. ^{1}H-NMR spectrum for data reported in Table 1, Entry 22.

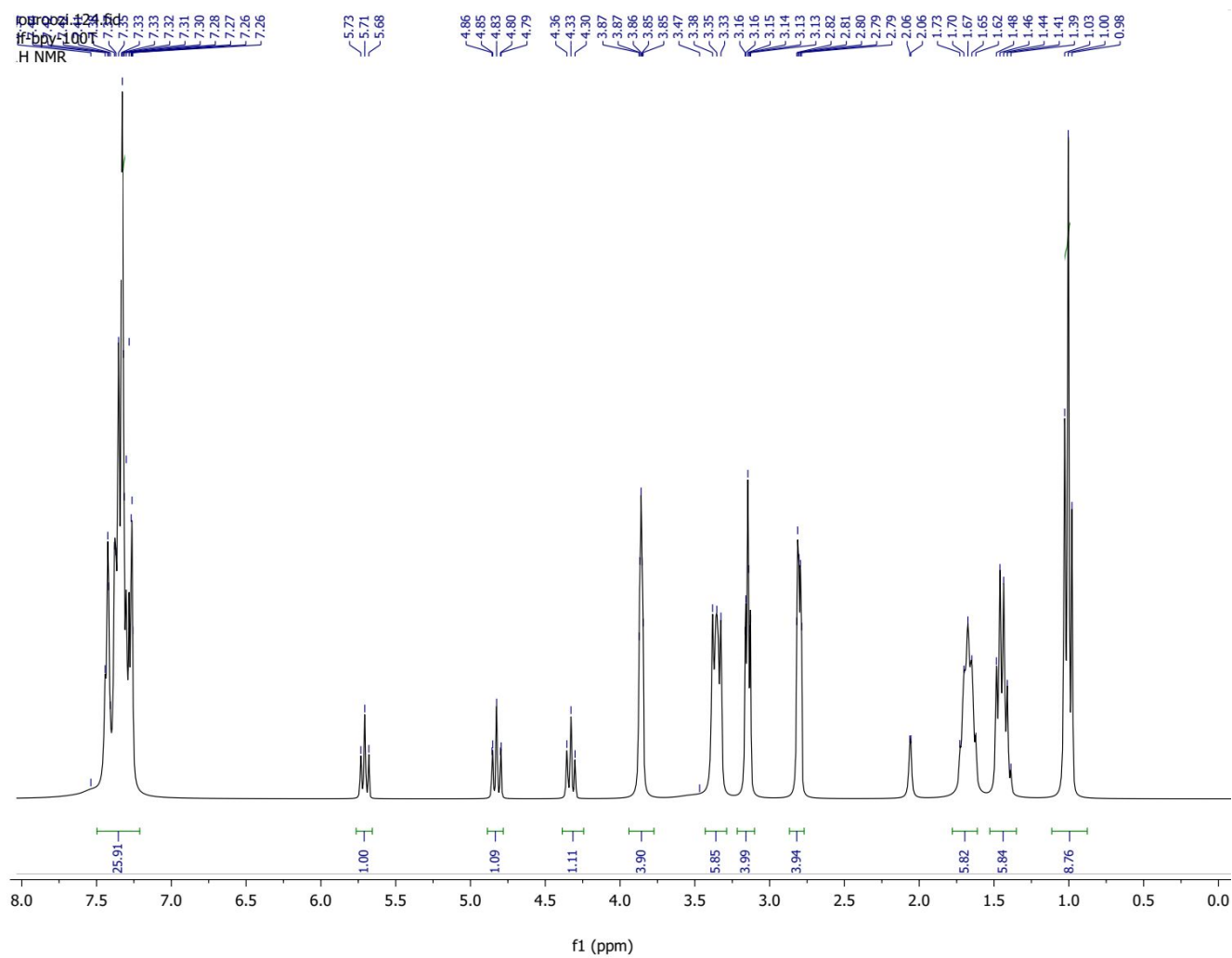**Figure S24.** ^{1}H-NMR spectrum for data reported in Table 2, Entry 1.

Table 2, Entry 2

Figure S25. ^{1}H-NMR spectrum for data reported in Table 2, Entry 2.

Figure S26. ^{1}H-NMR spectrum for data reported in Table 2, Entry 3.

Figure S27. ^{1}H-NMR spectrum for data reported in Table 2, Entry 4.

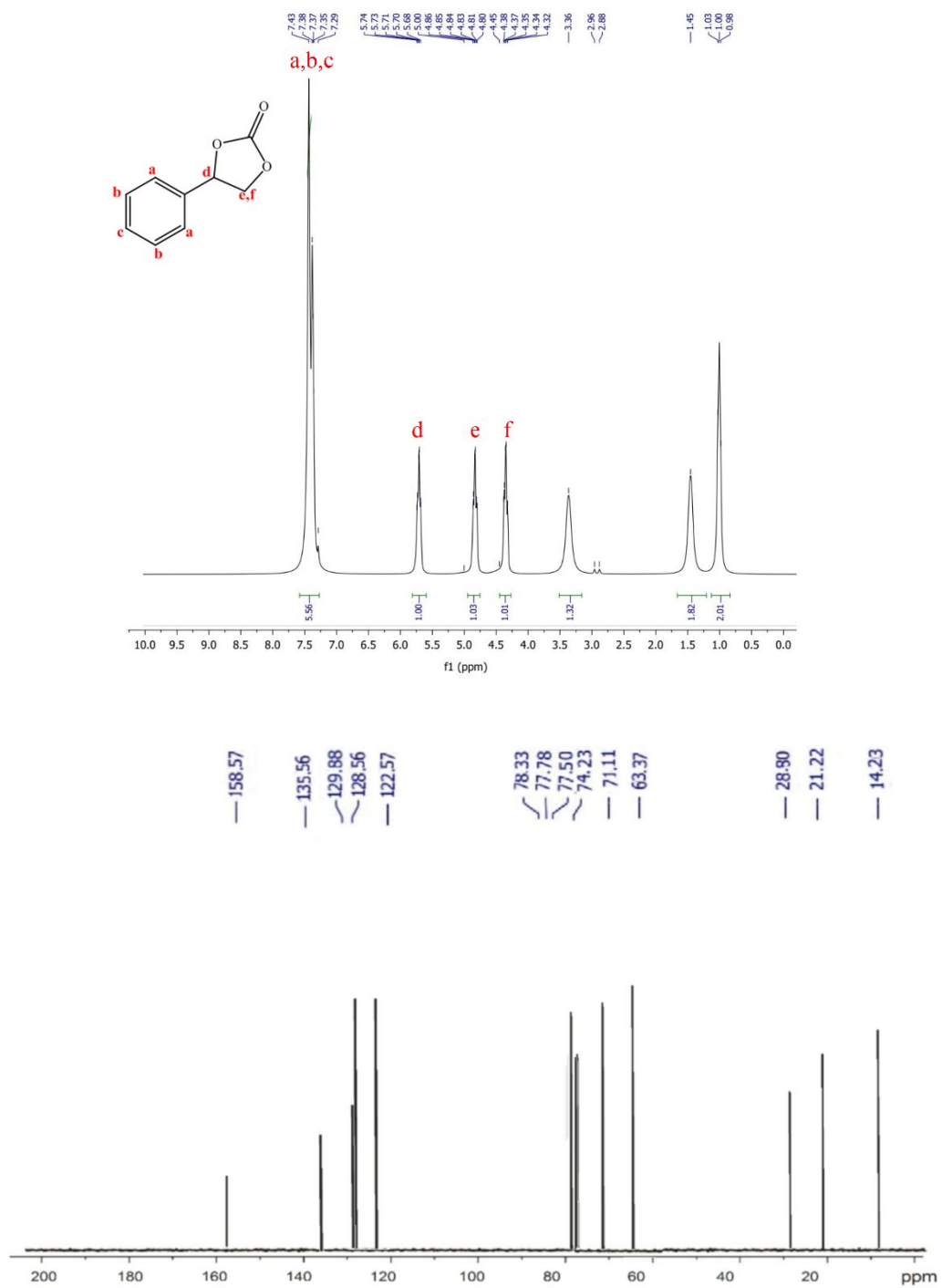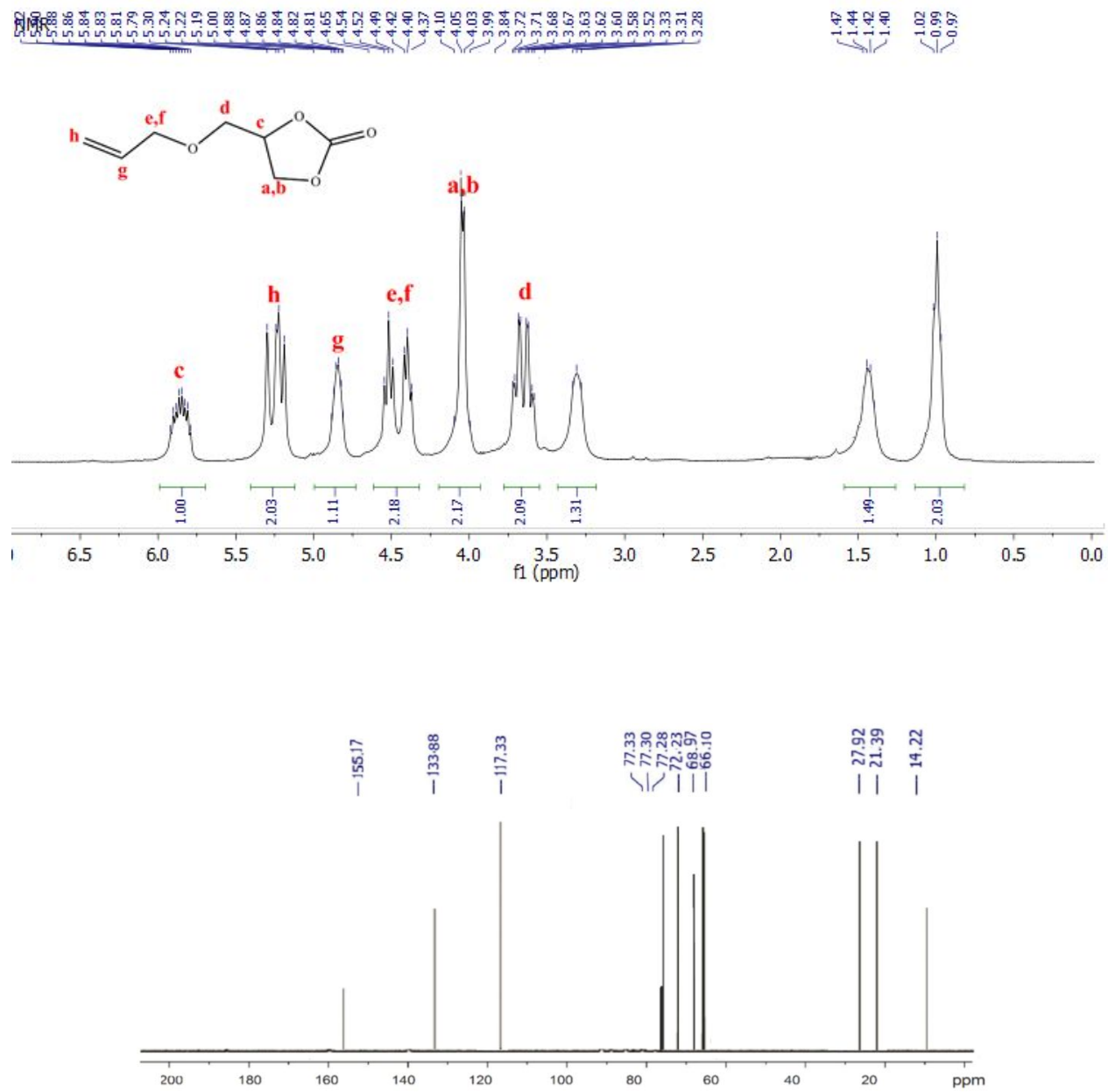**Figure S28.** ^{1}H-NMR spectrum for data reported in Table 2, Entry 5.

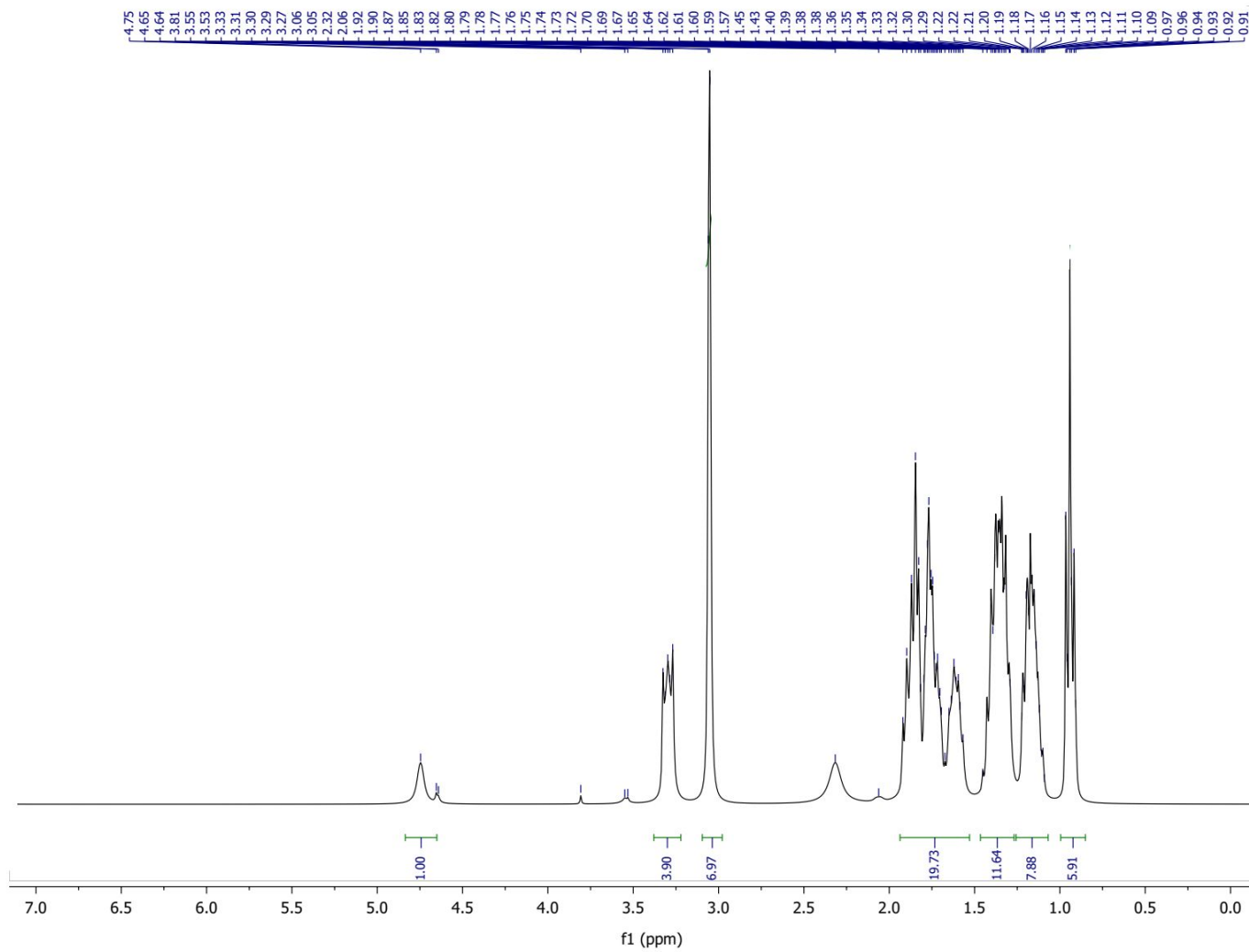**Figure S29.** ^{1}H-NMR spectrum for data reported in Table 2, Entry 6.

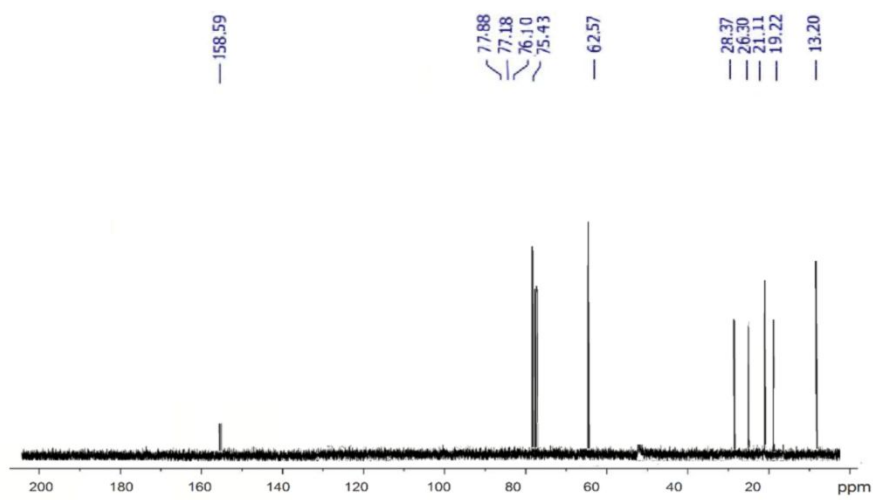**Figure S30.** ^{1}H-NMR spectrum for data reported in Table 2, Entry 7.

Figure S31. ^{1}H-NMR spectrum for data reported in Table 2, Entry 8.

Figure S32. ^{1}H-NMR spectrum for data reported in Table 2, Entry 9.

S37

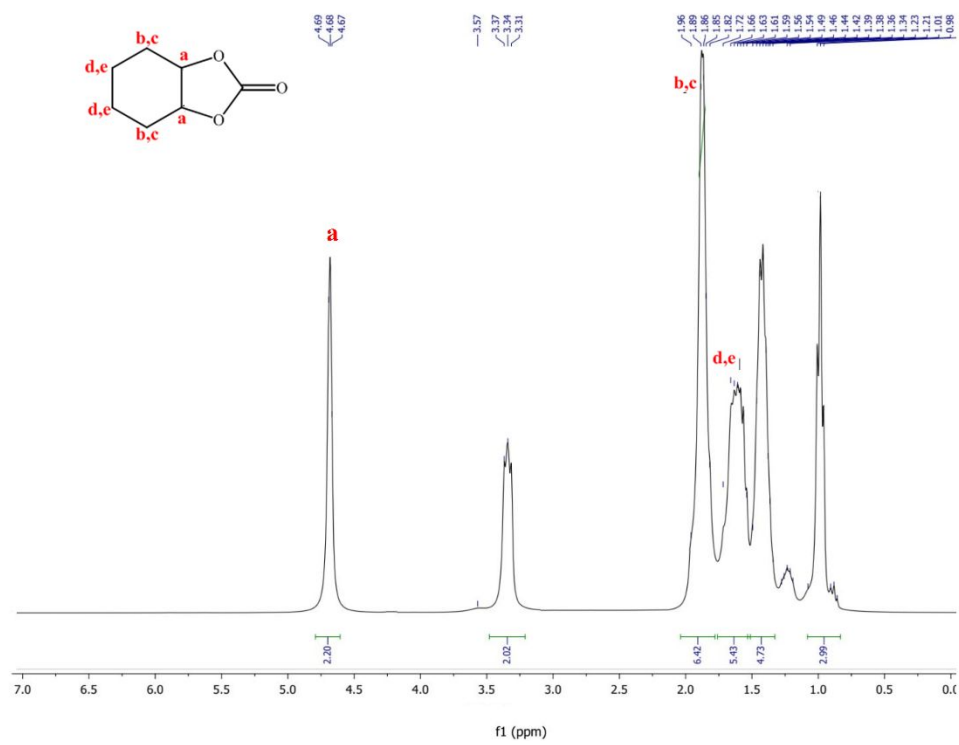**Figure S33.** ^{1}H-NMR spectrum for data reported in Table 4, Entry 3.

Figure S34. ^{1}H-NMR and ^{13}C-NMR spectrum for data reported in Table 4, Entry 4.

Figure S35. ^{1}H-NMR spectrum for data reported in Table 4, Entry 5.

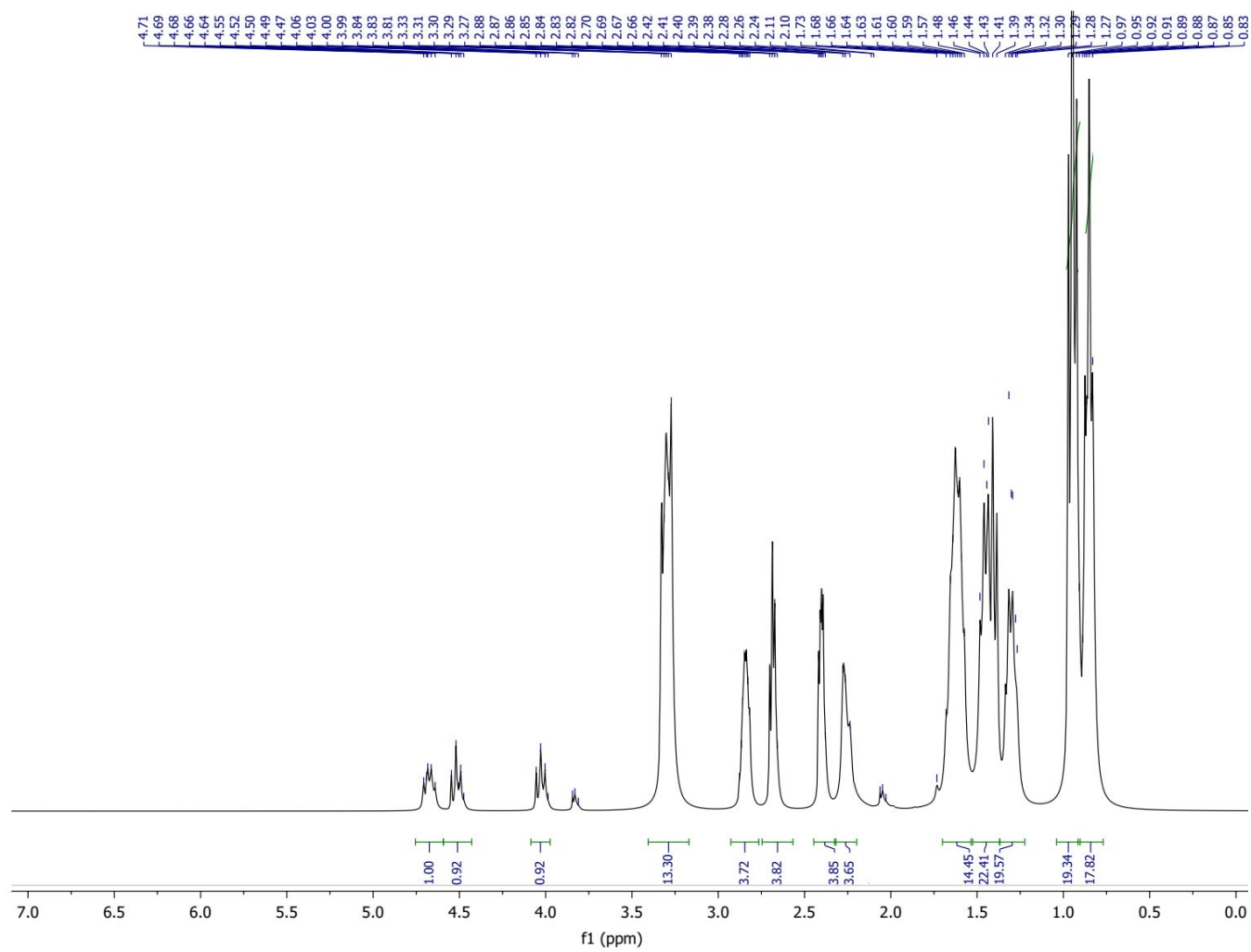**Figure S36.** ^{1}H-NMR and ^{13}C-NMR spectrum for data reported in Table 4, Entry 6.

Figure S37. ^{1}H-NMR spectrum for data reported in Table 4, Entry 7.

Figure S38. ¹H-NMR and ¹³C-NMR spectrum for data reported in Table 4, Entry 8.

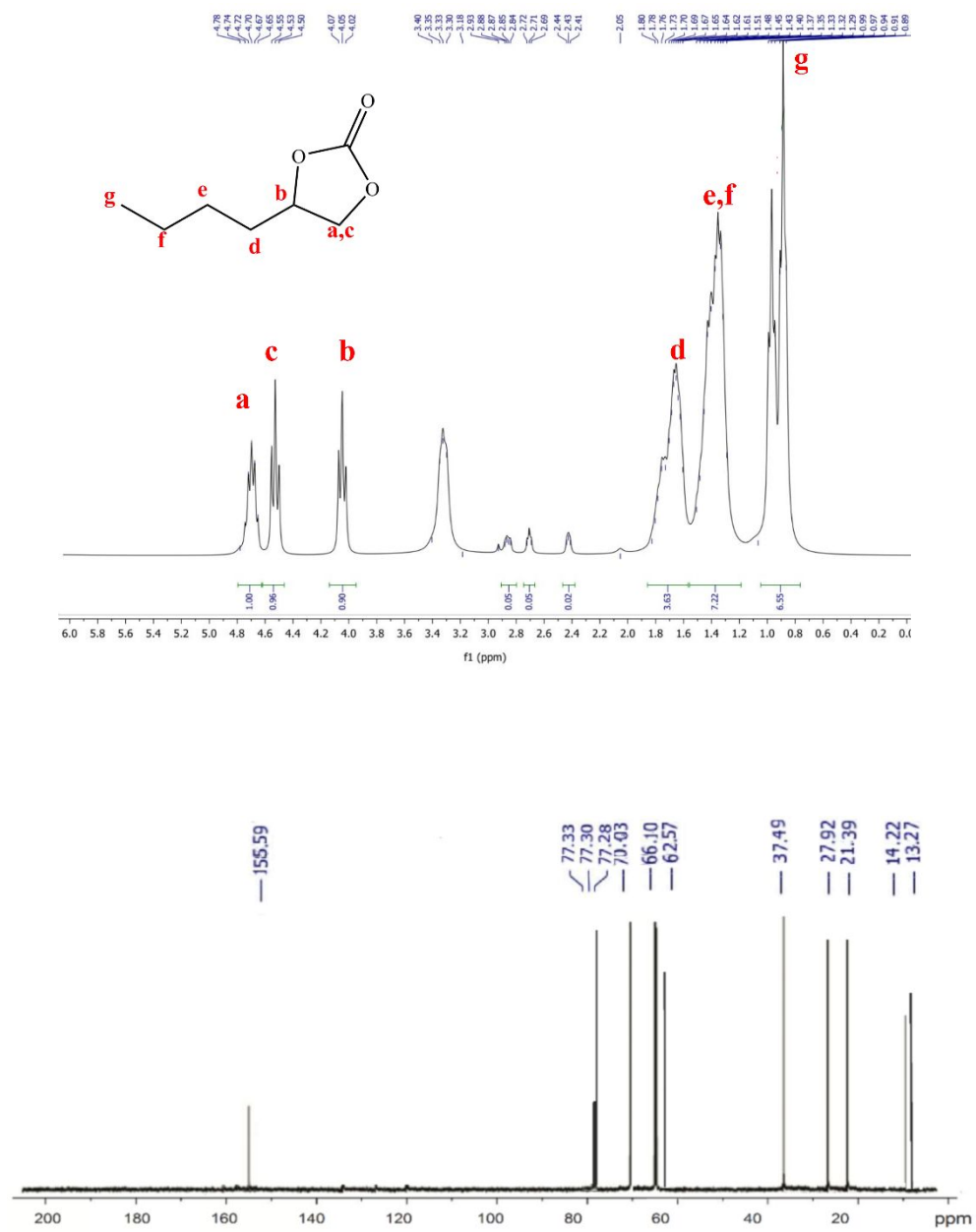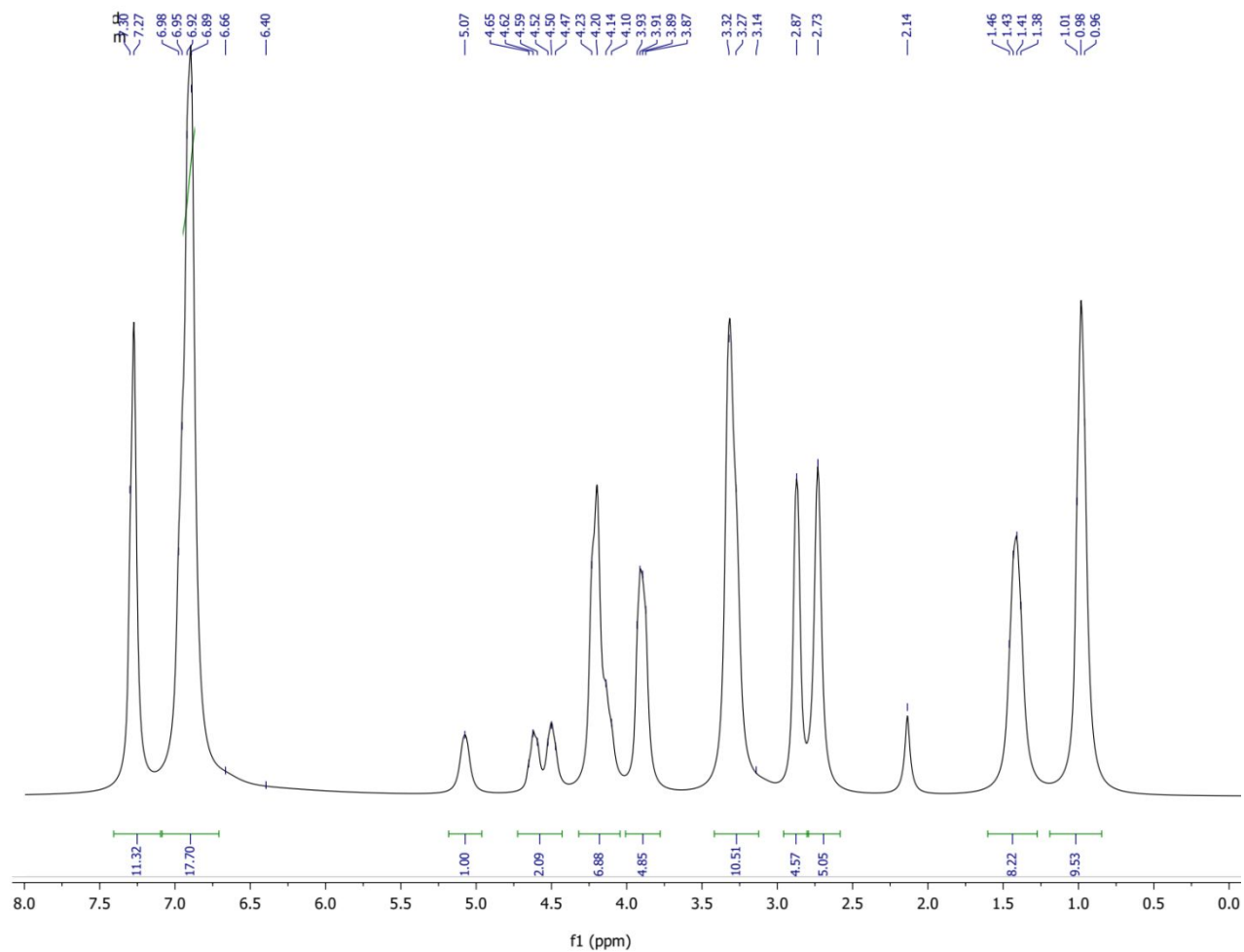**Figure S39.** ^{1}H-NMR spectrum for data reported in Table 4, Entry 9.

Table 4, Entry 10

Figure S40. ¹H-NMR and ¹³C-NMR spectrum for data reported in Table 4, Entry 10.

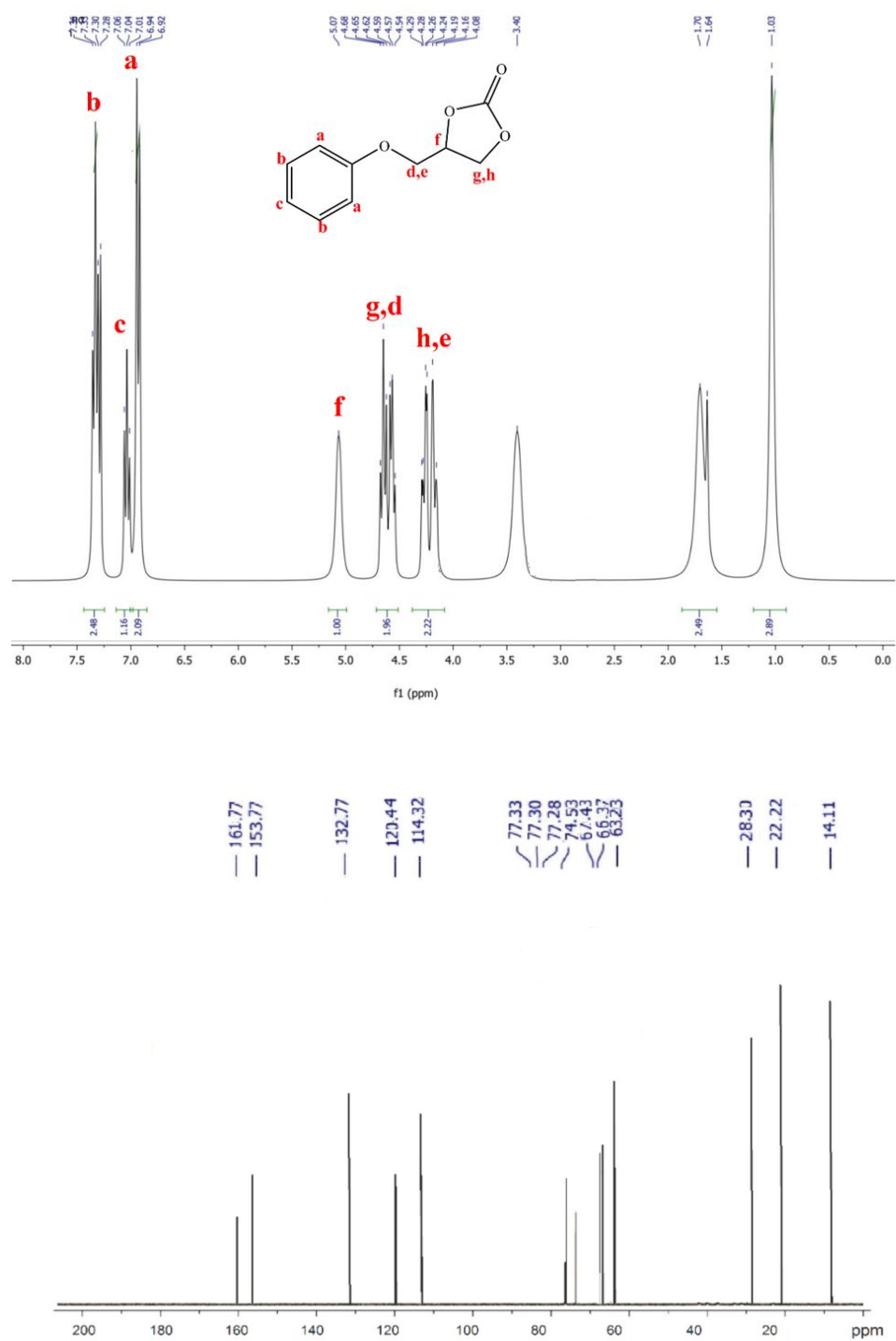**Figure S41.** ^{1}H-NMR spectrum for data reported in Table 4, Entry 11.

Figure S42. ^{1}H-NMR and ^{13}C-NMR spectrum for data reported in Table 4, Entry 12.
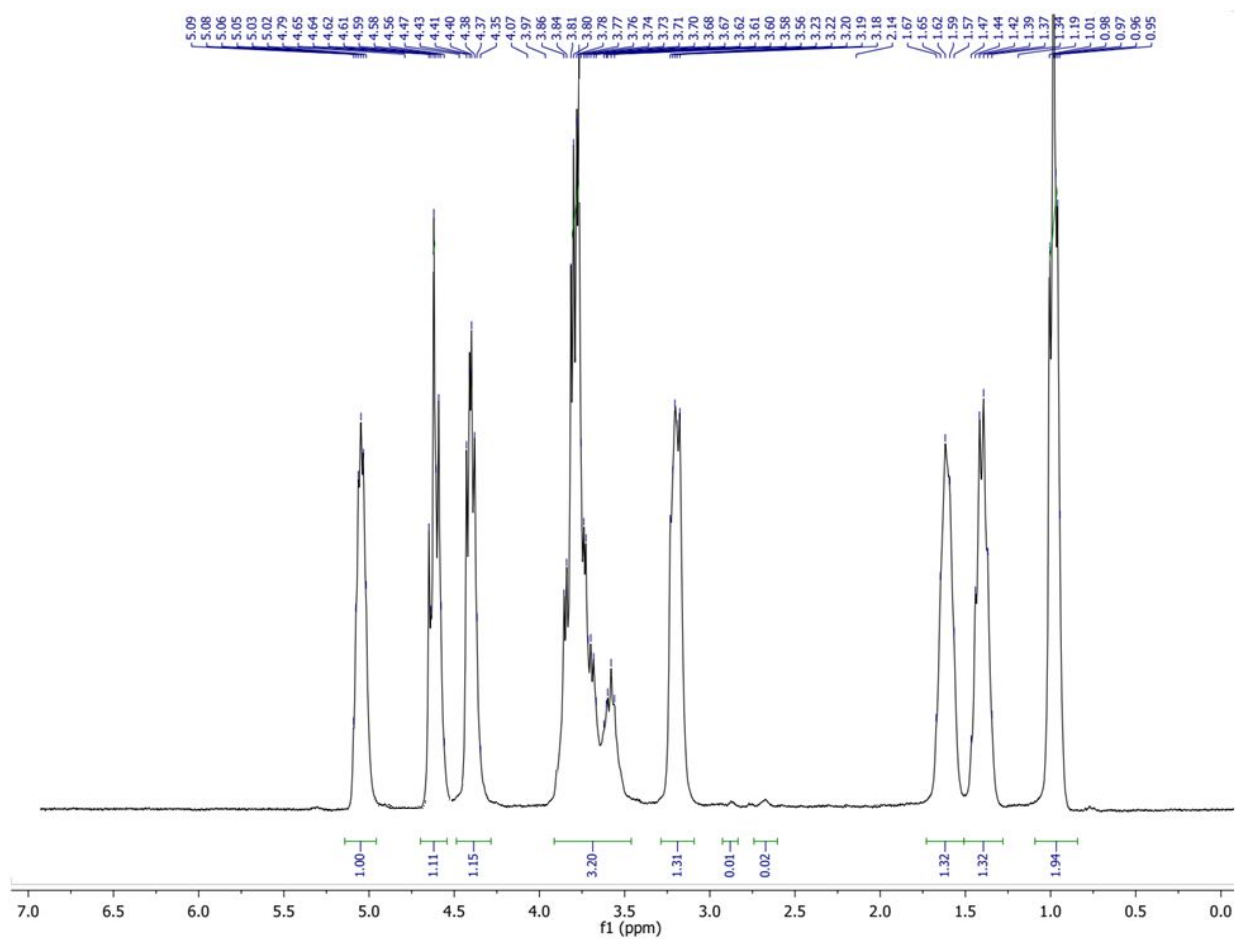
Figure S43. ^{1}H-NMR spectrum recyclability tests, Run 1.
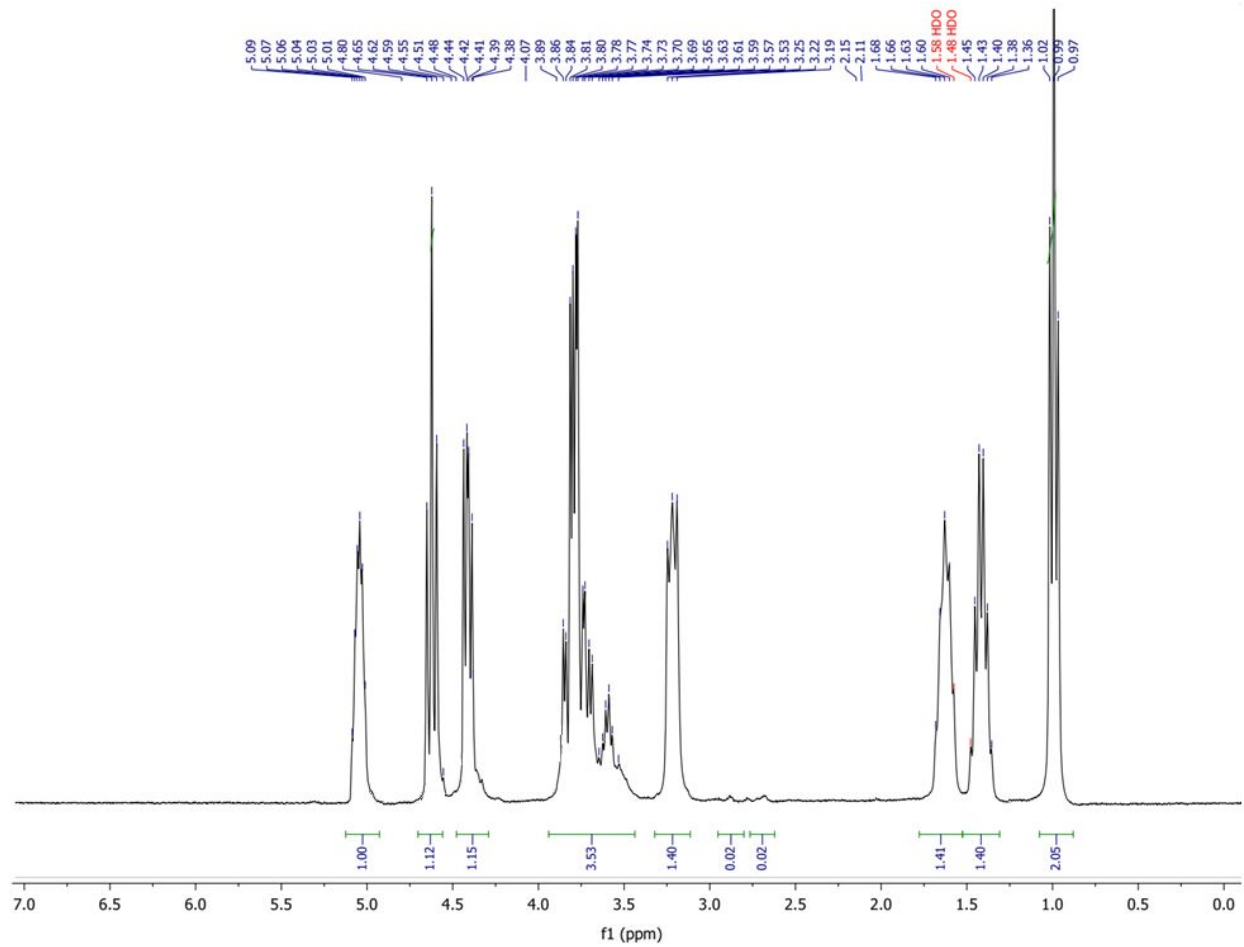
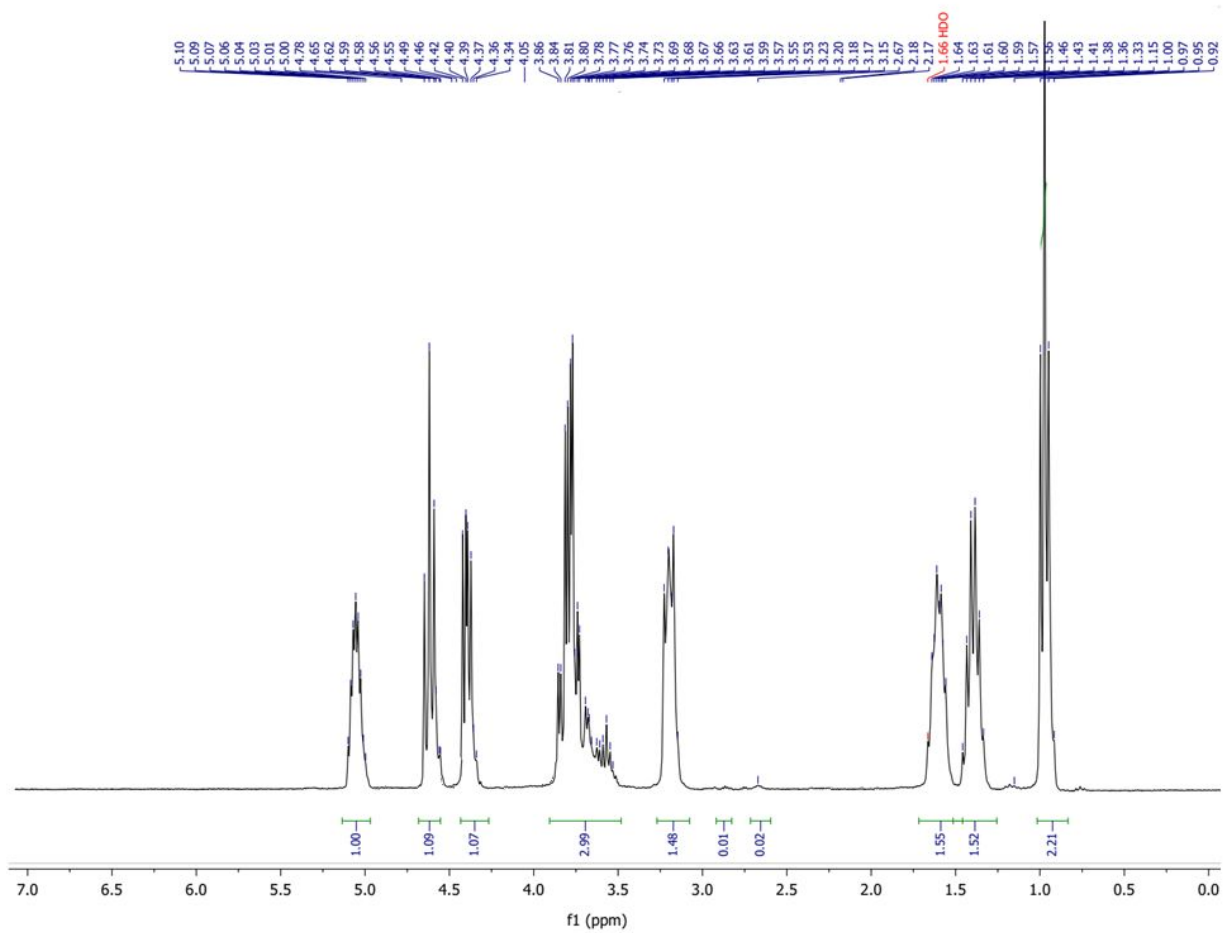**Figure S44.** ^{1}H-NMR spectrum recyclability tests, Run 2.

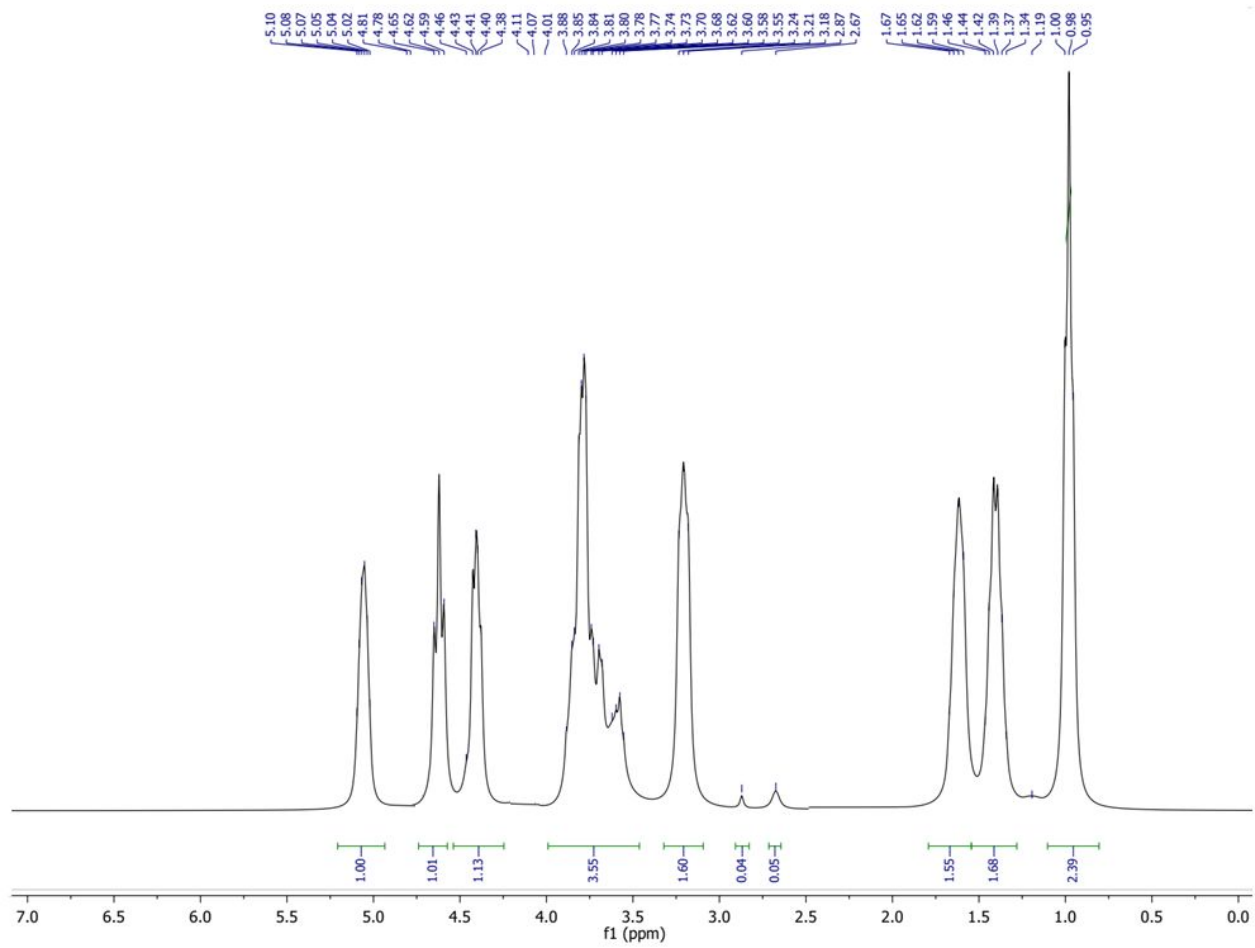**Figure S45.** ^{1}H-NMR spectrum recyclability tests, Run 3.
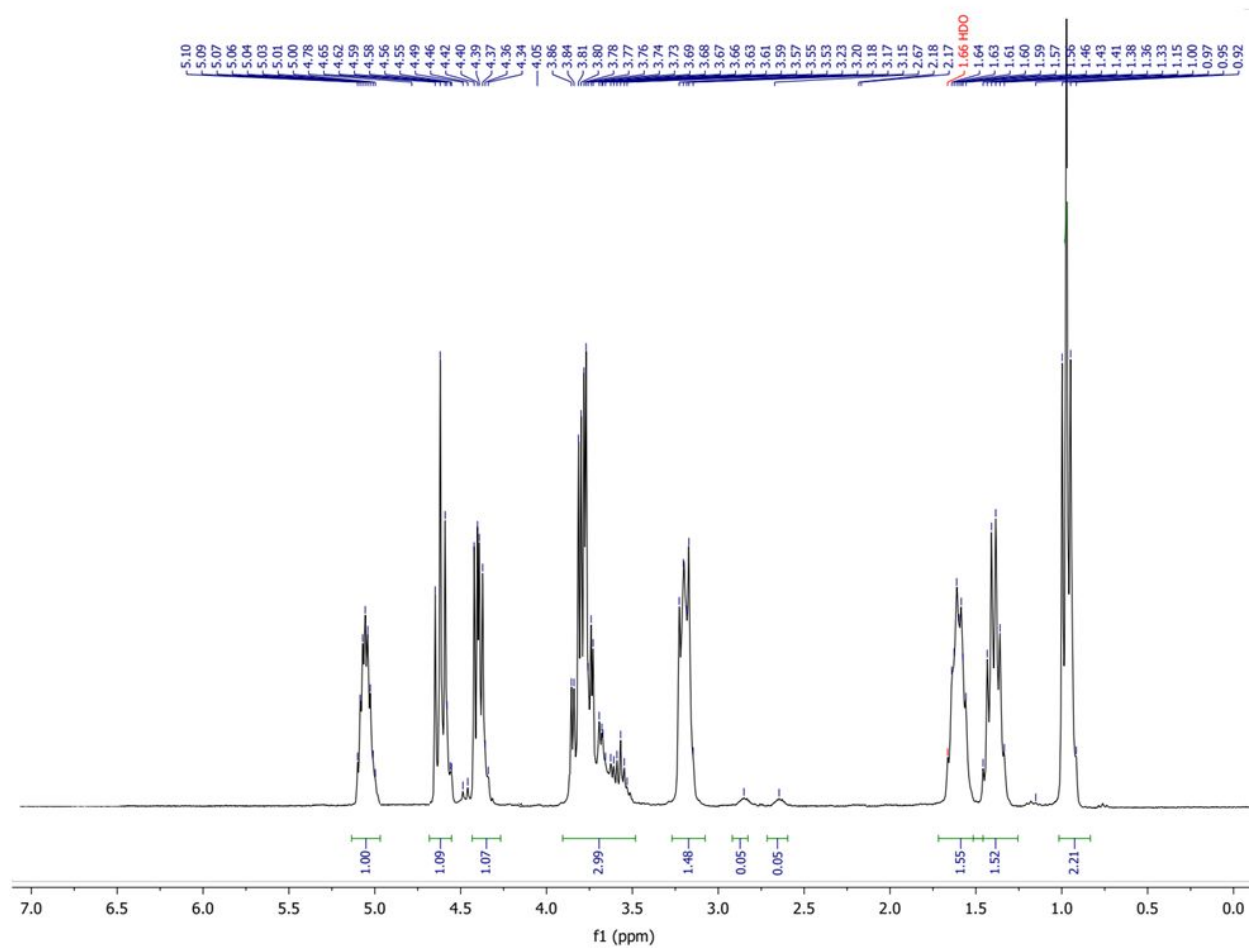
Figure S46. ^{1}H-NMR spectrum recyclability tests, Run 4.

Figure S47. ^{1}H-NMR spectrum recyclability tests, Run 5.