

α -Glucosidase Inhibitors from Two Mangrove-Derived Actinomycetes

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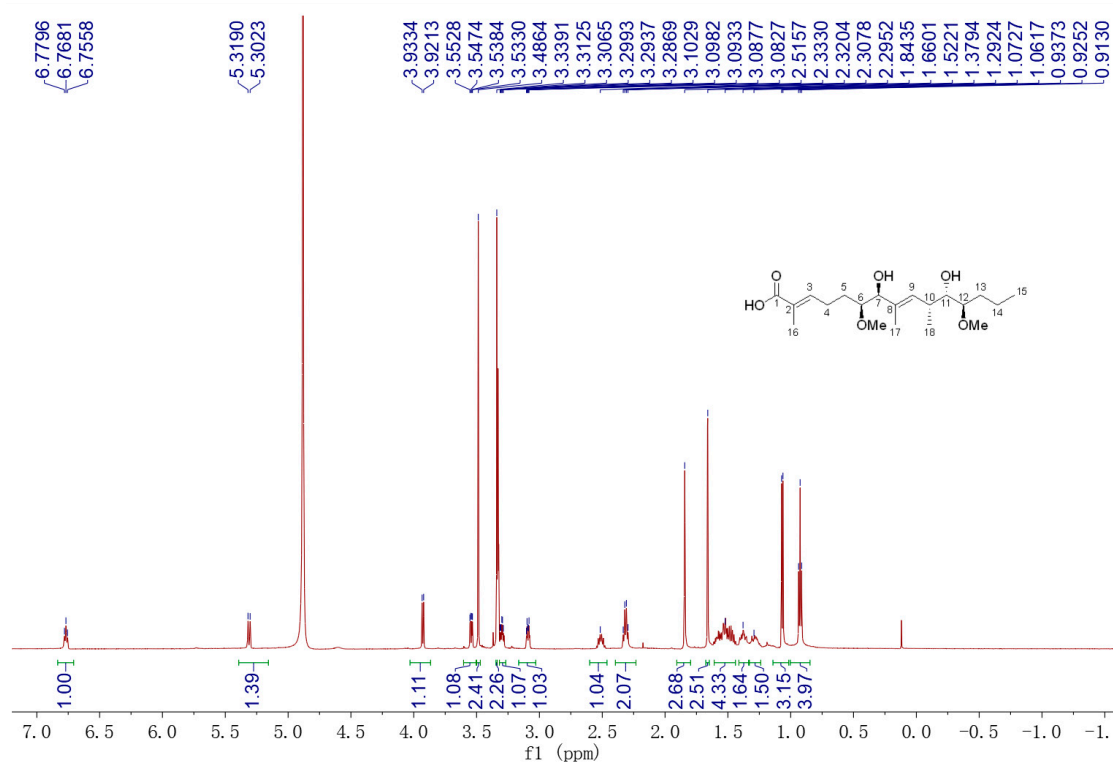


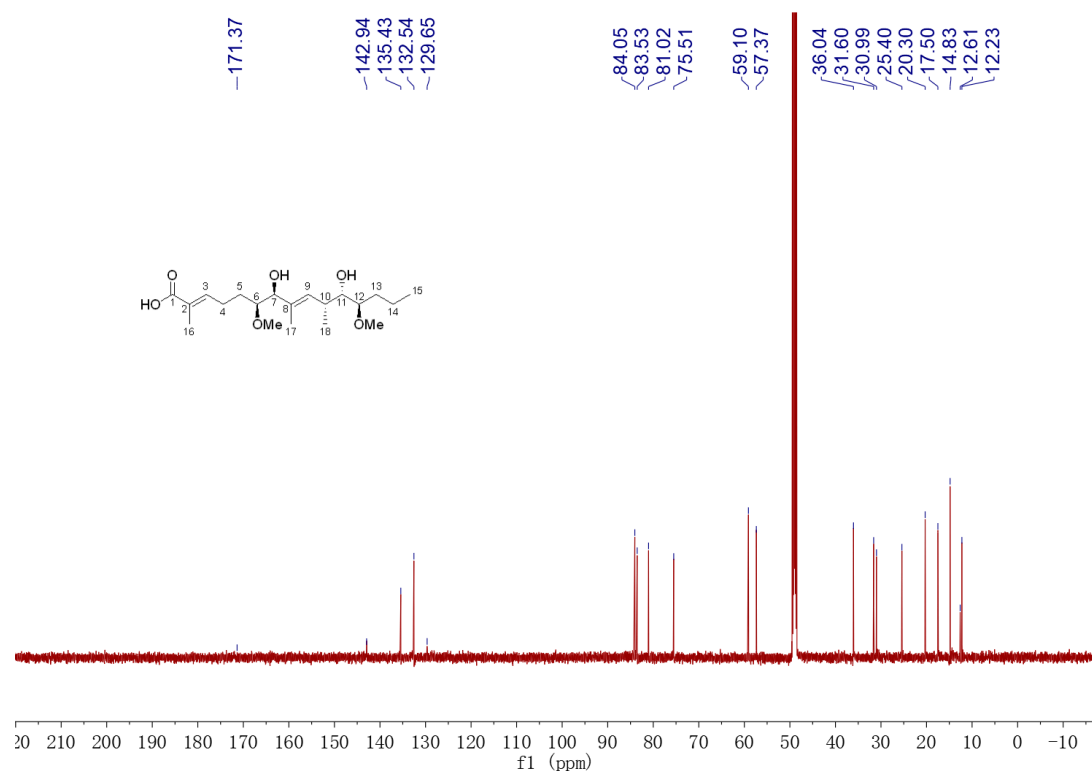
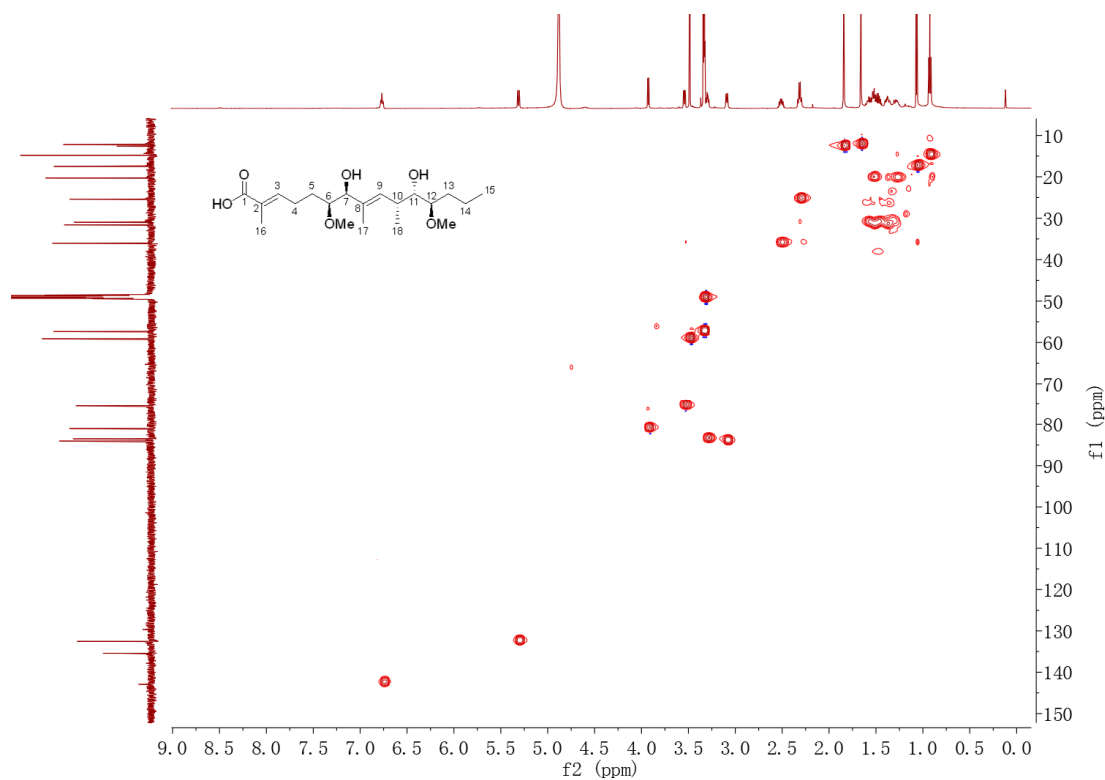
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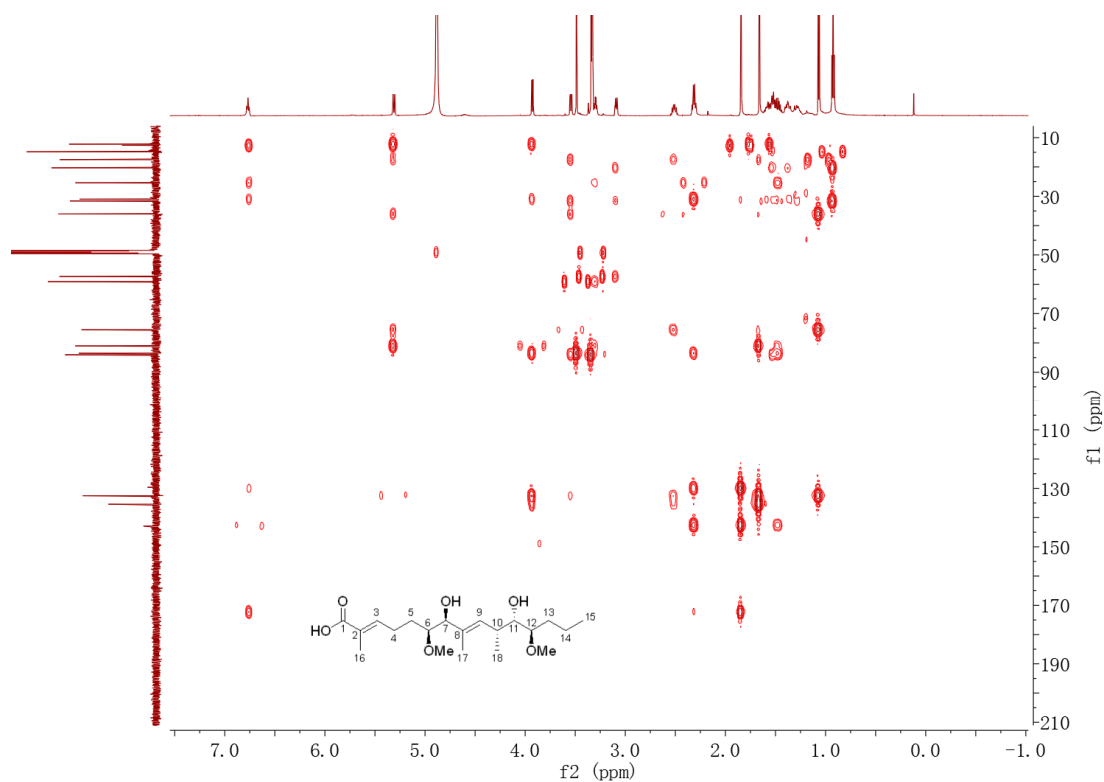
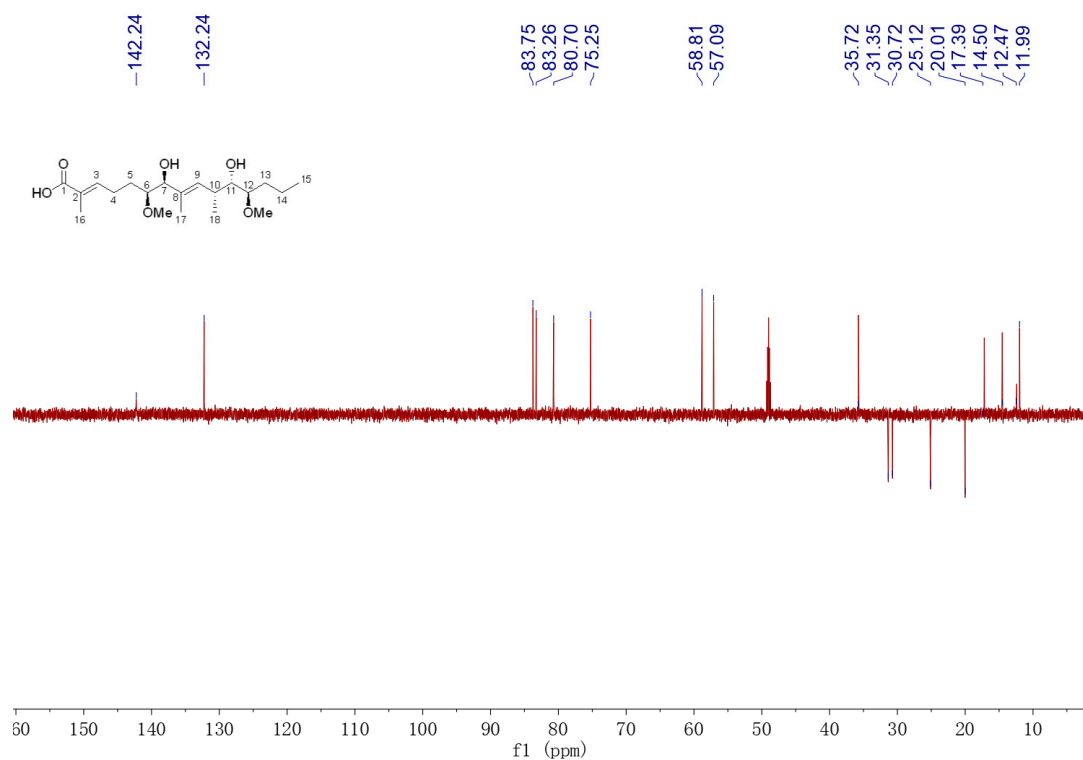
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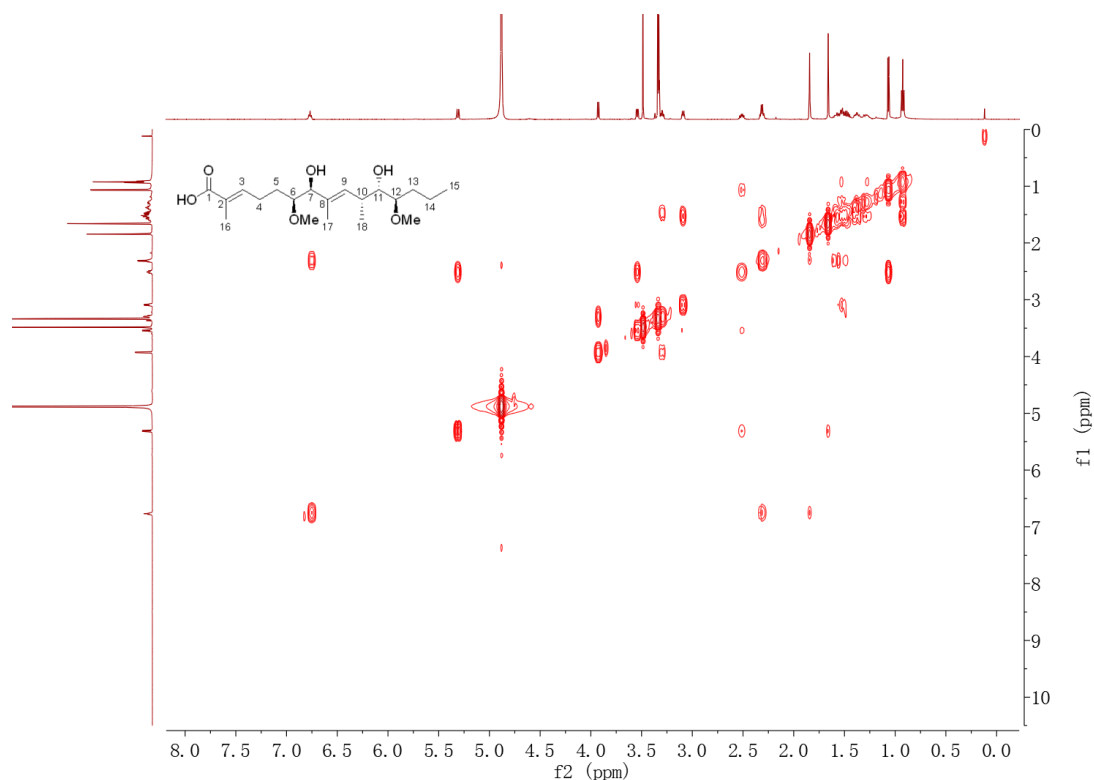
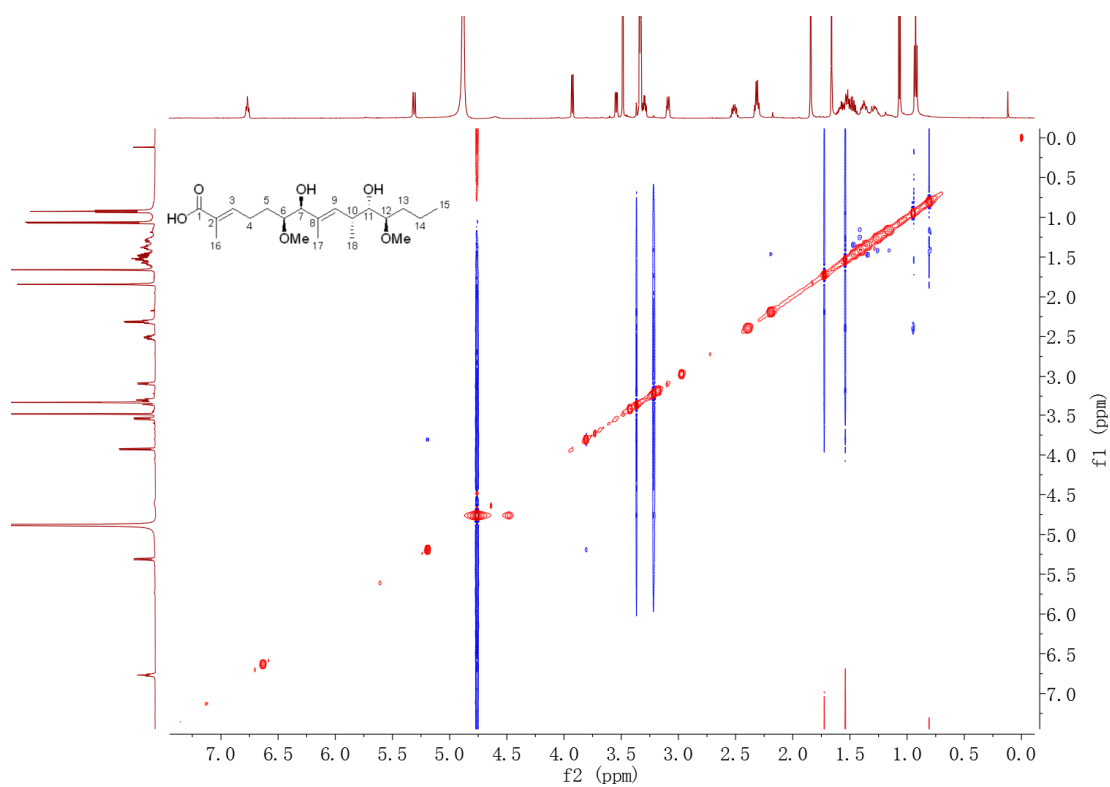
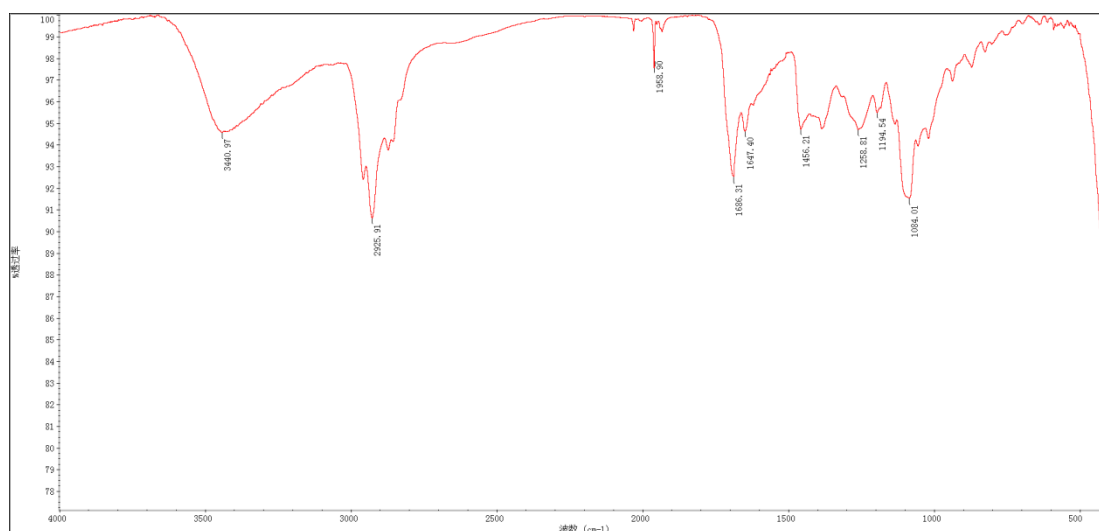
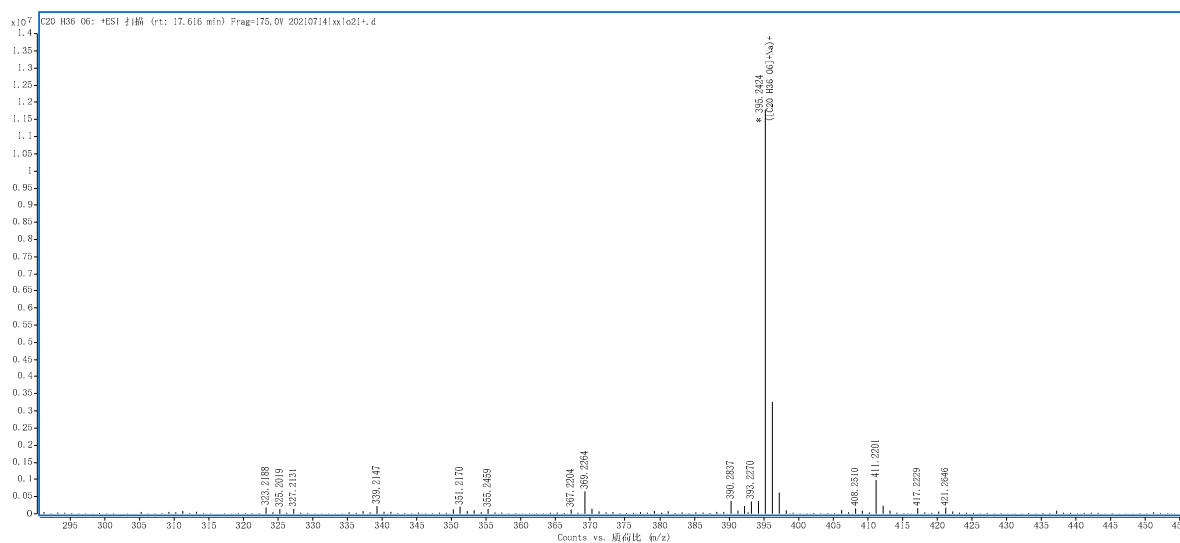
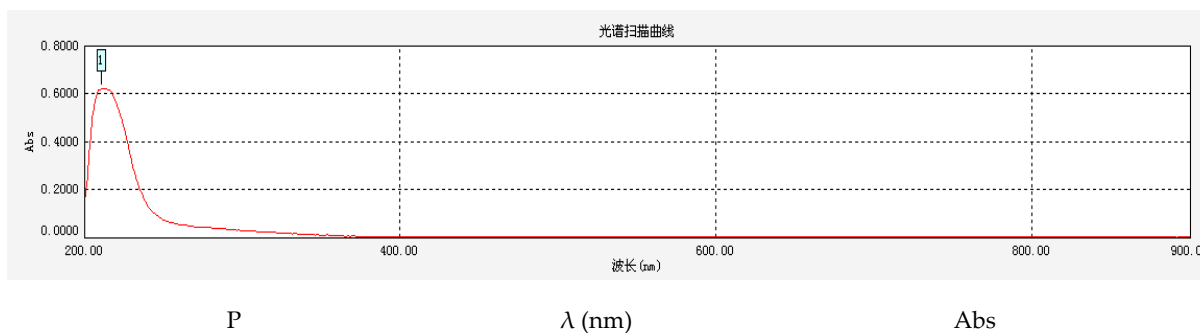
Figure S1e. DEPT spectrum of **1** in CD₃OD.**Figure S1f.** ¹H-¹H COSY spectrum of **1** in CD₃OD.

Figure S1g. NOESY spectrum of **1** in CD₃OD.**Figure S1h.** The IR (KBr disc) spectrum of **1**.

Formula (M)	Ion Formula	m/z	Calc m/z	Diff (ppm)	DBE
C ₂₀ H ₃₆ O ₆	C ₂₀ H ₃₆ NaO ₆	395.2424	395.2404	-4.67	3

Figure S1i. The HR-ESI-MS spectroscopic data of **1**.

1

215

0.6198

Figure S1j. UV spectrum of 1.

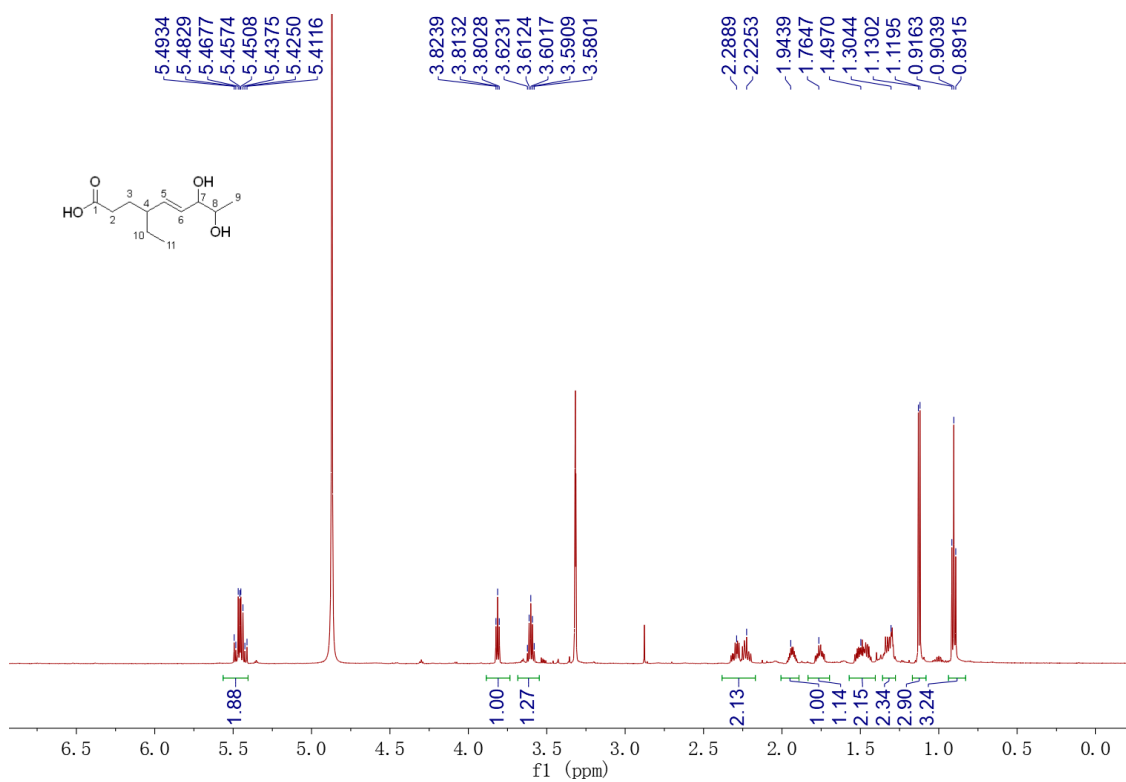
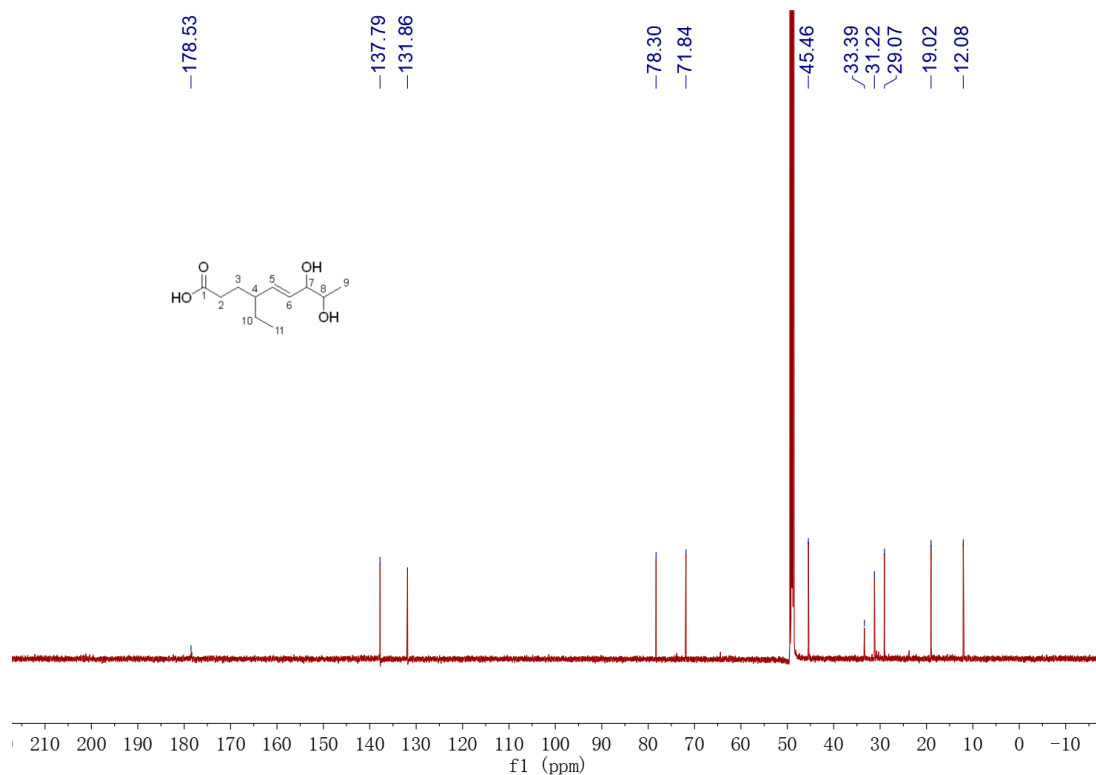
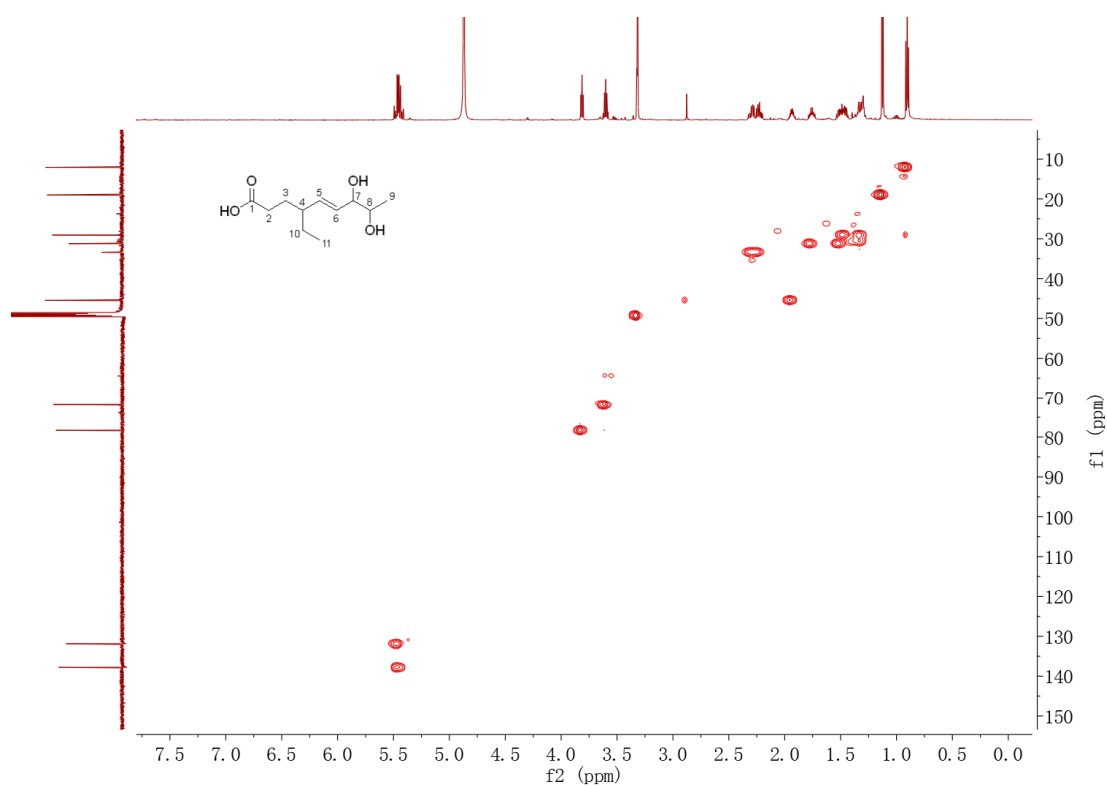
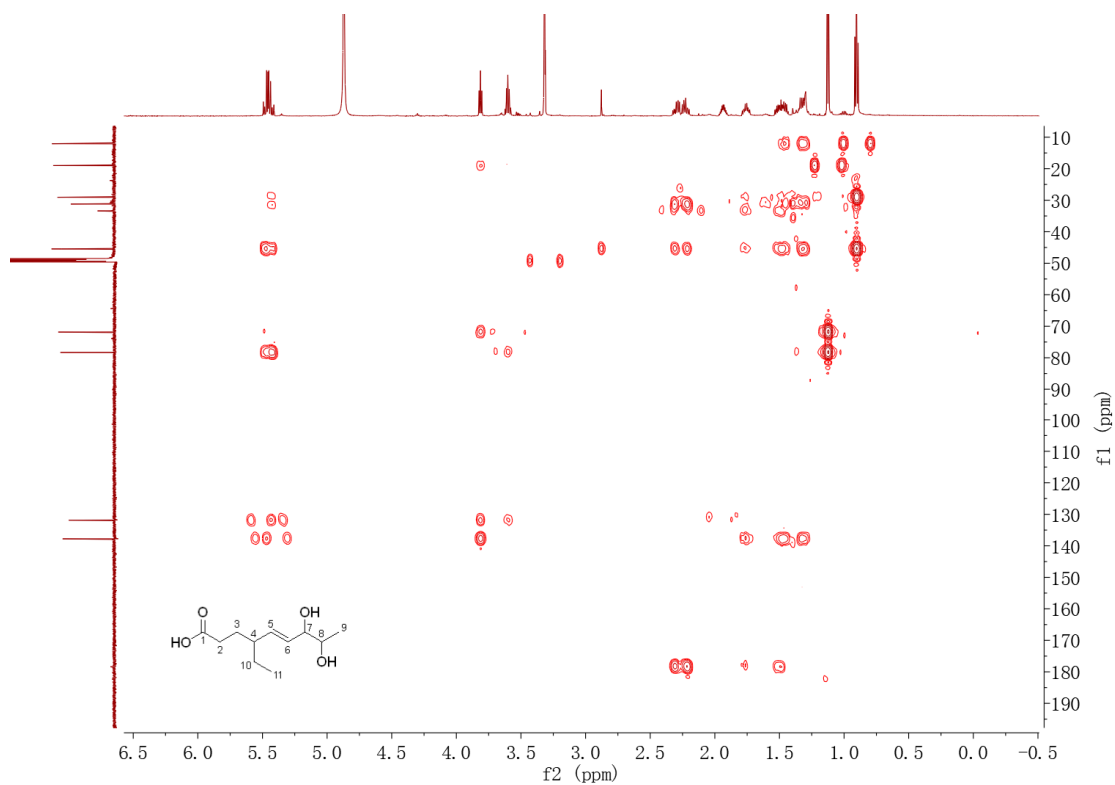
Figure S2a. ¹H NMR spectrum of 2 in CD₃OD.

Figure S2b. ^{13}C NMR spectrum of **2** in CD_3OD .**Figure S2c.** HSQC spectrum of **2** in CD_3OD .**Figure S2d.** HMBC spectrum of **2** in CD_3OD .

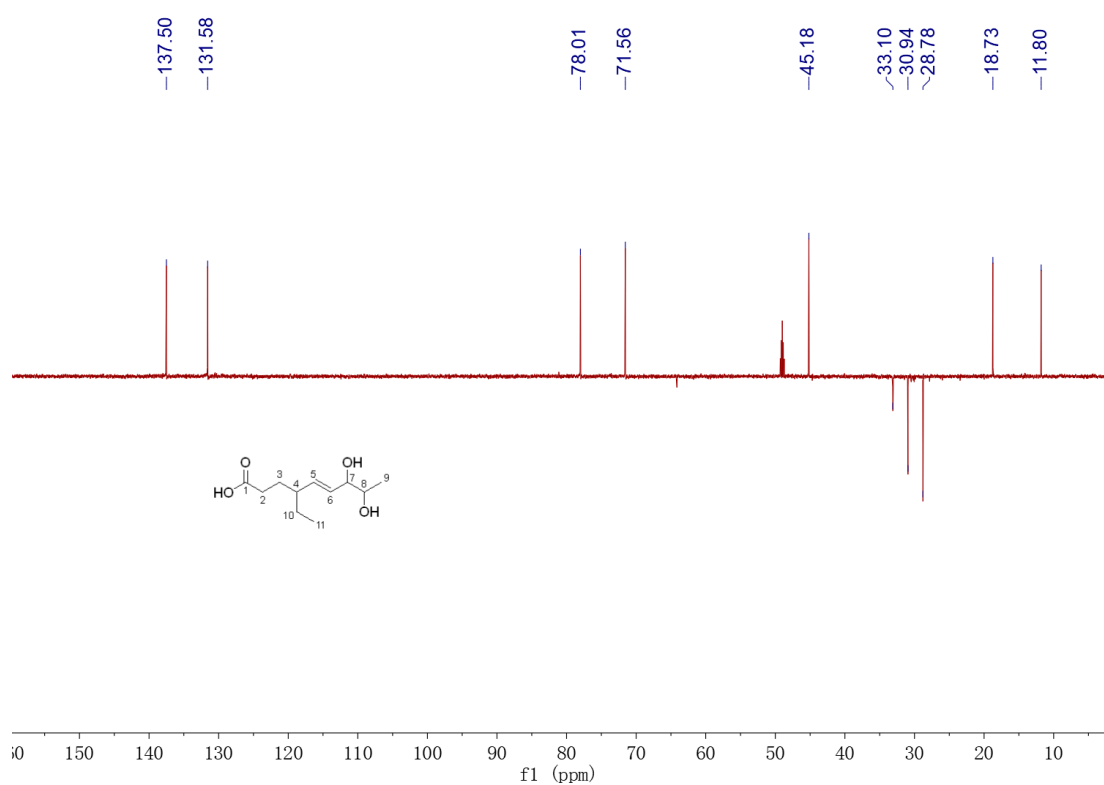


Figure S2e. DEPT spectrum of 2 in CD₃OD.

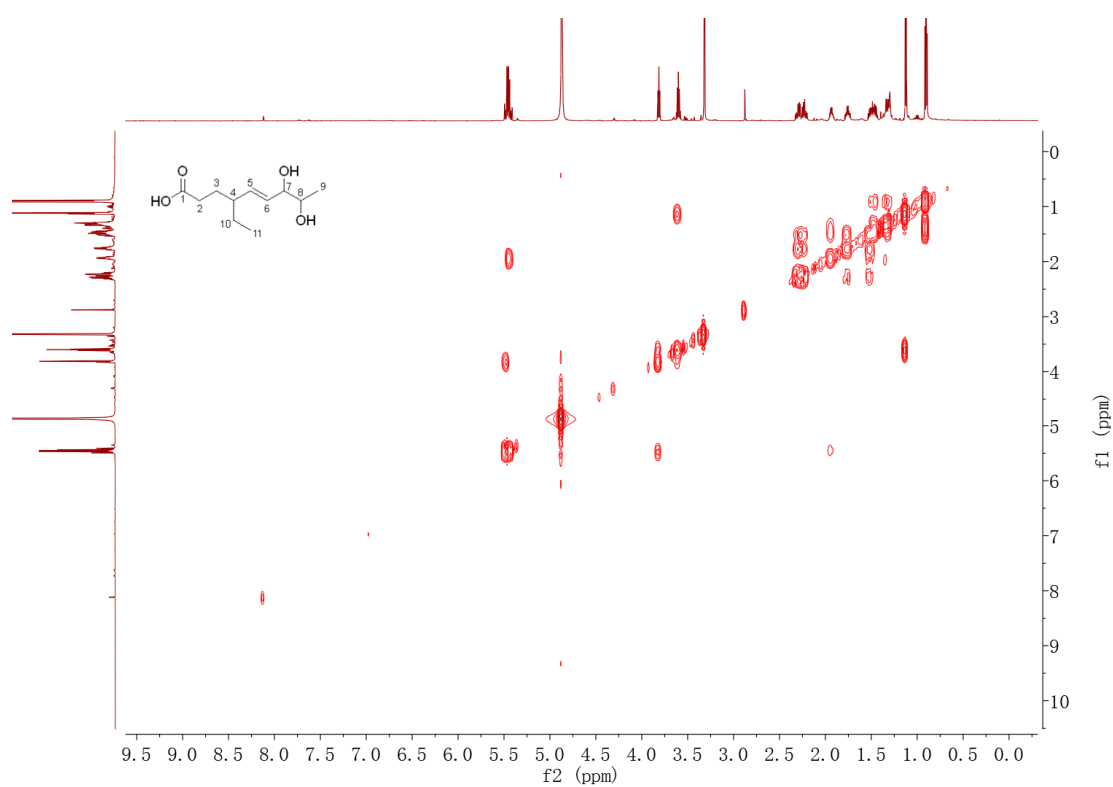


Figure S2f. ¹H-¹H COSY spectrum of 2 in CD₃OD.

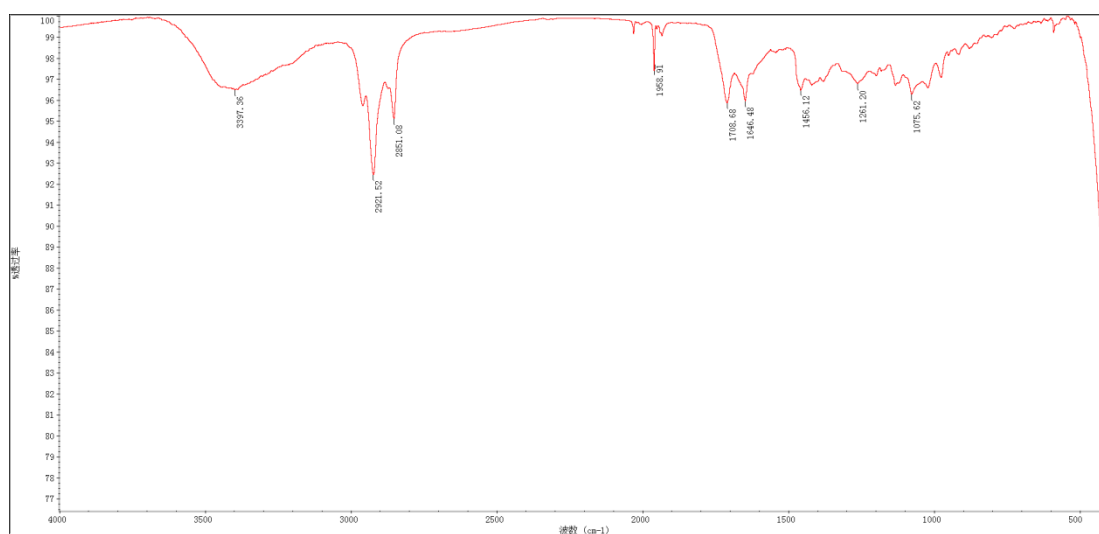
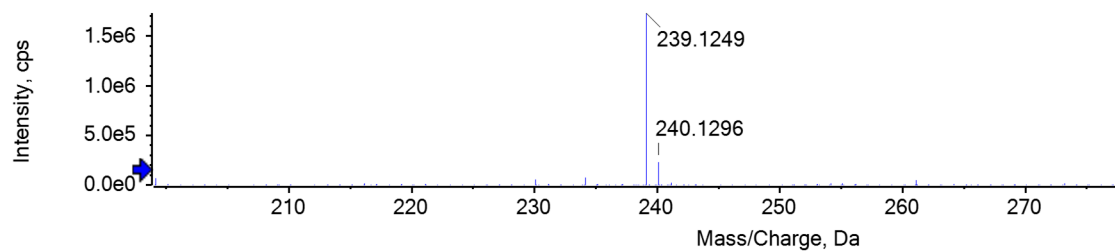


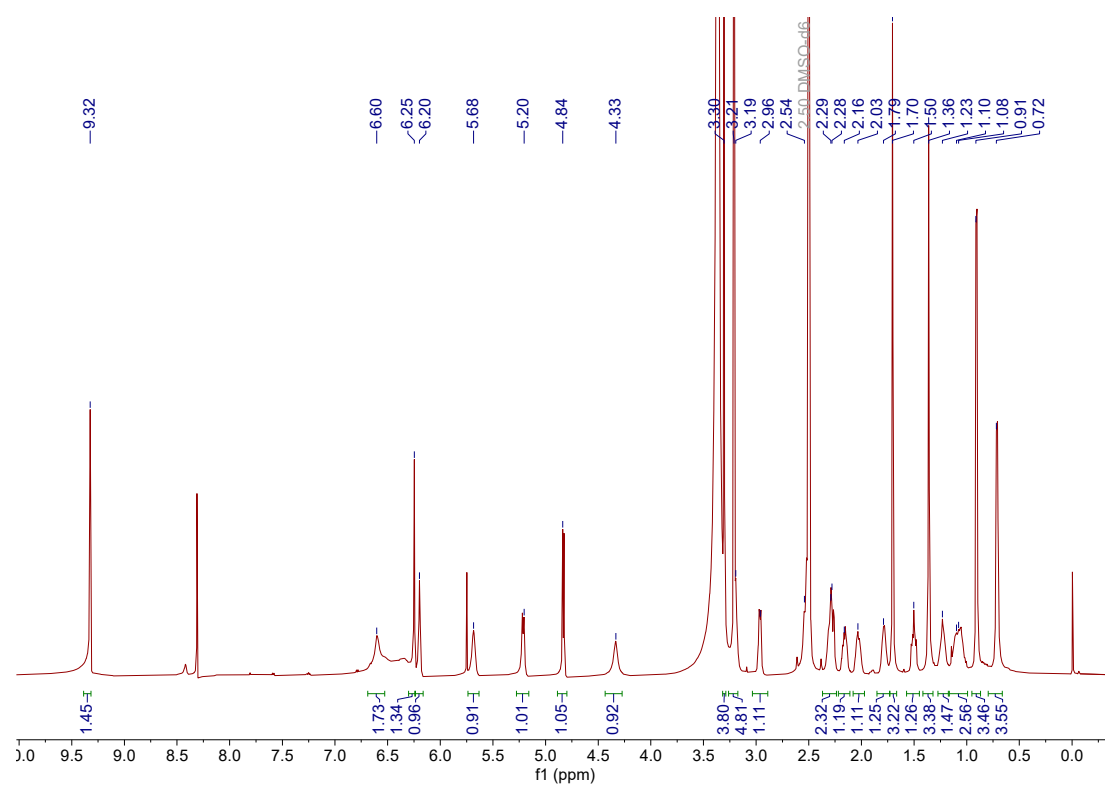
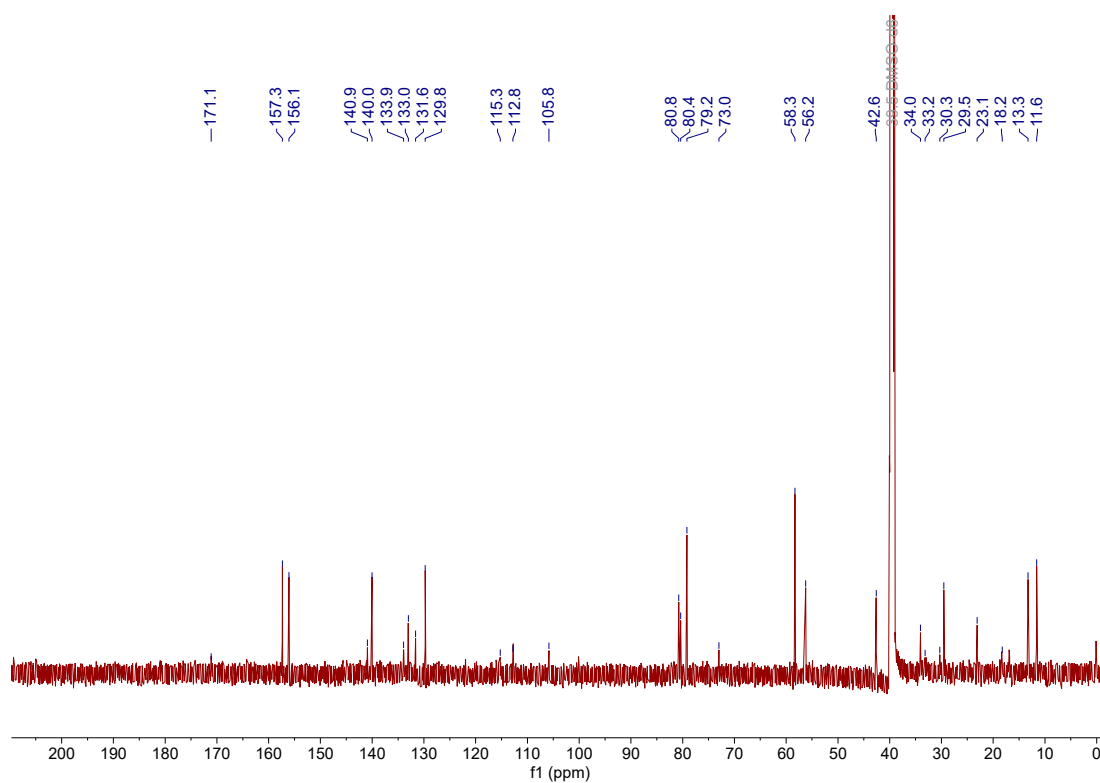
Figure S2g. The IR (KBr disc) spectrum of **2**.

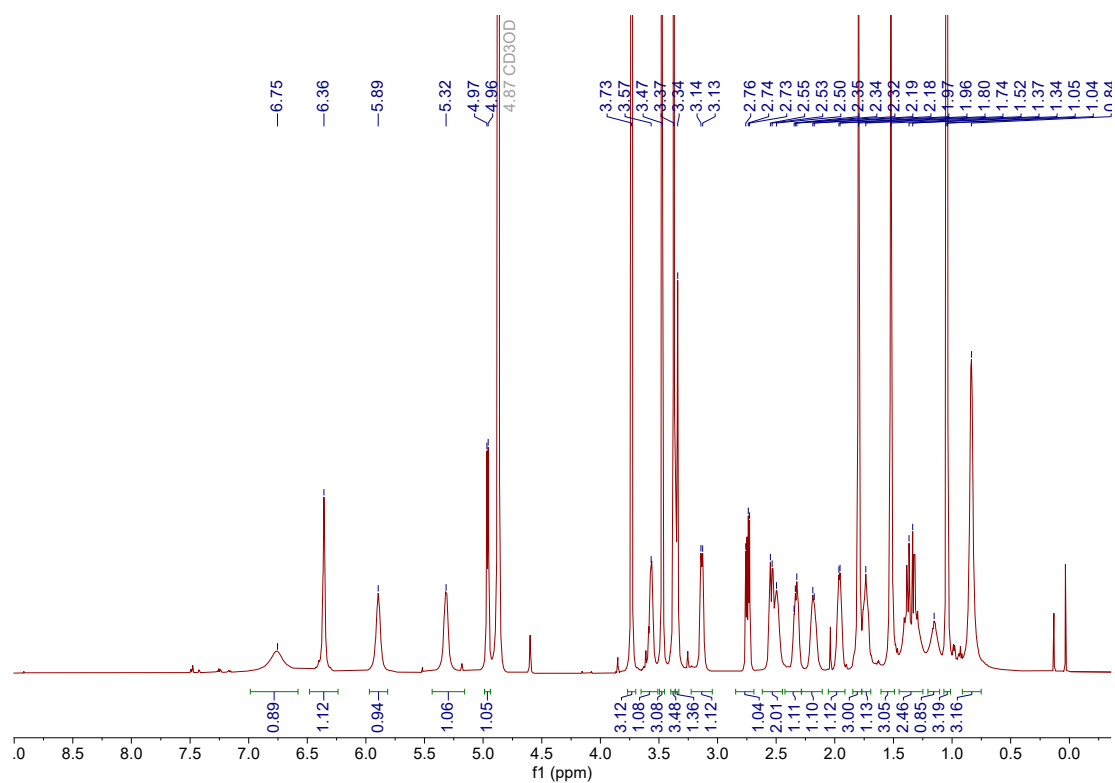
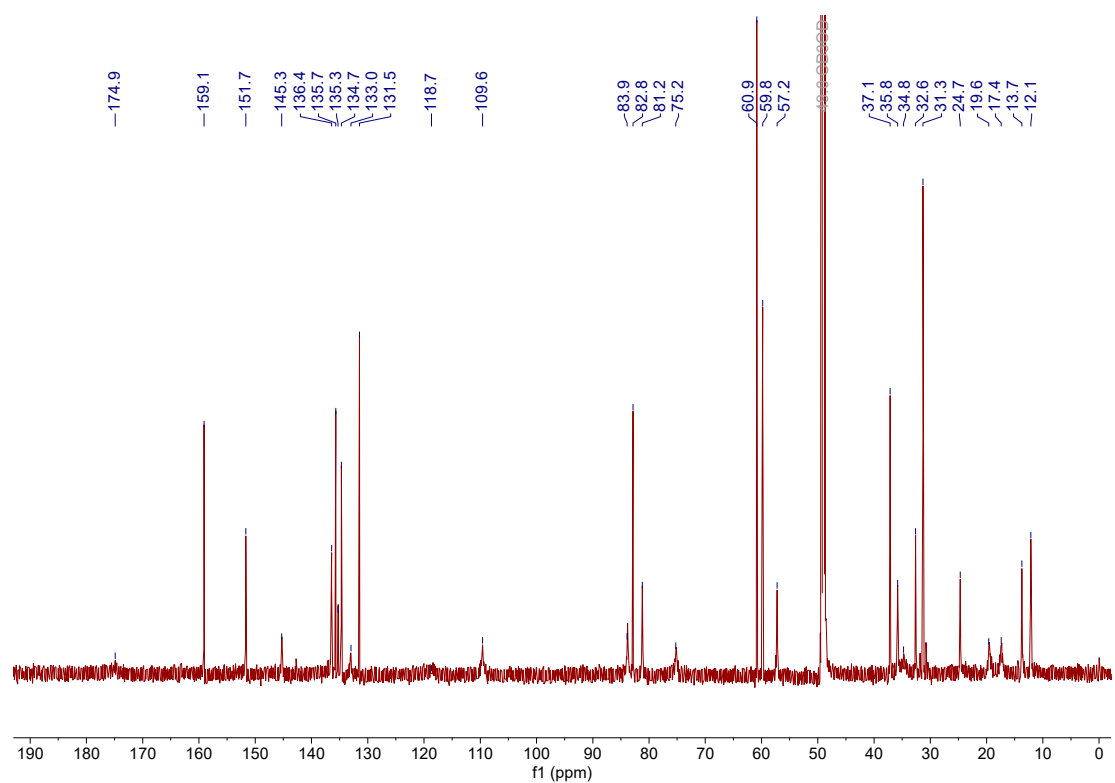
Spectrum from 20211216.wiff2 (sample 14) - B-06-S2 187, +TOF MS (100 - 1000) from 5.925 min

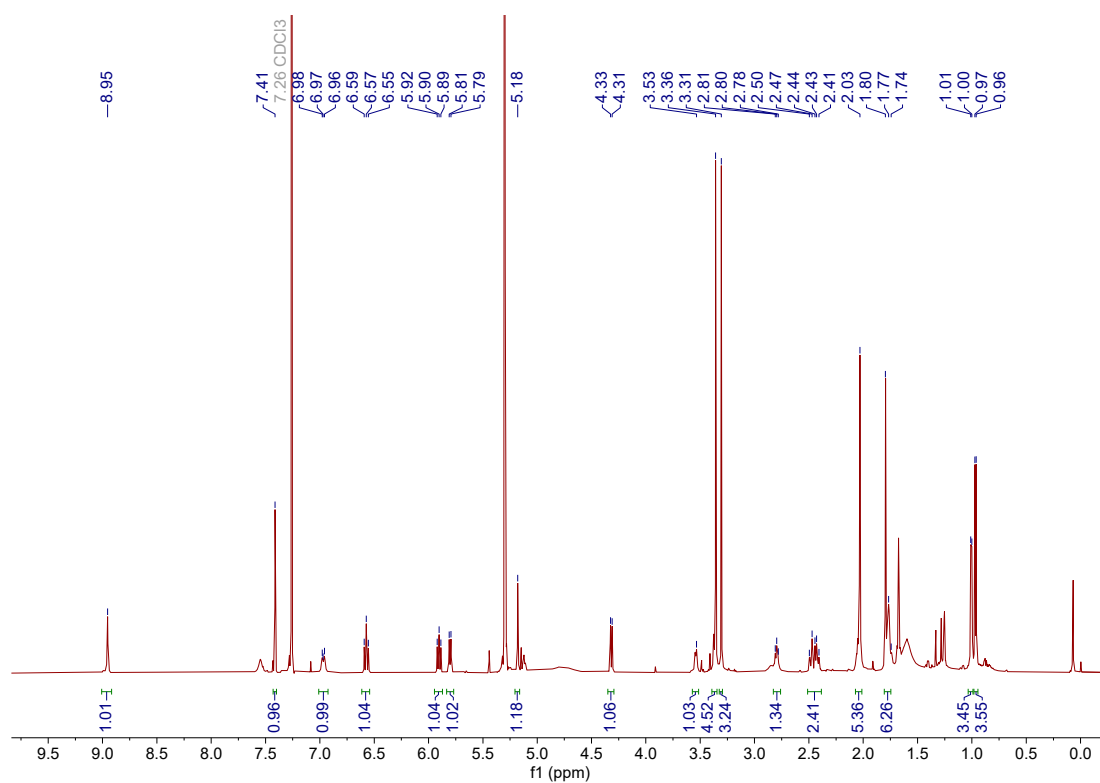
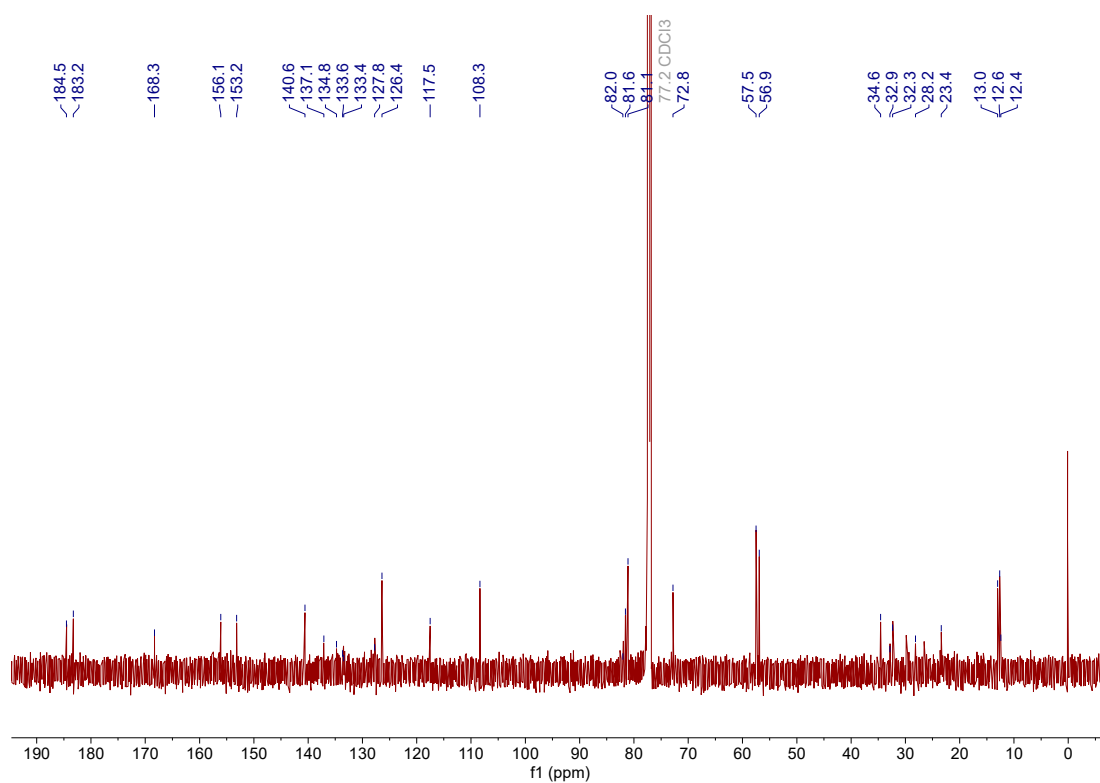


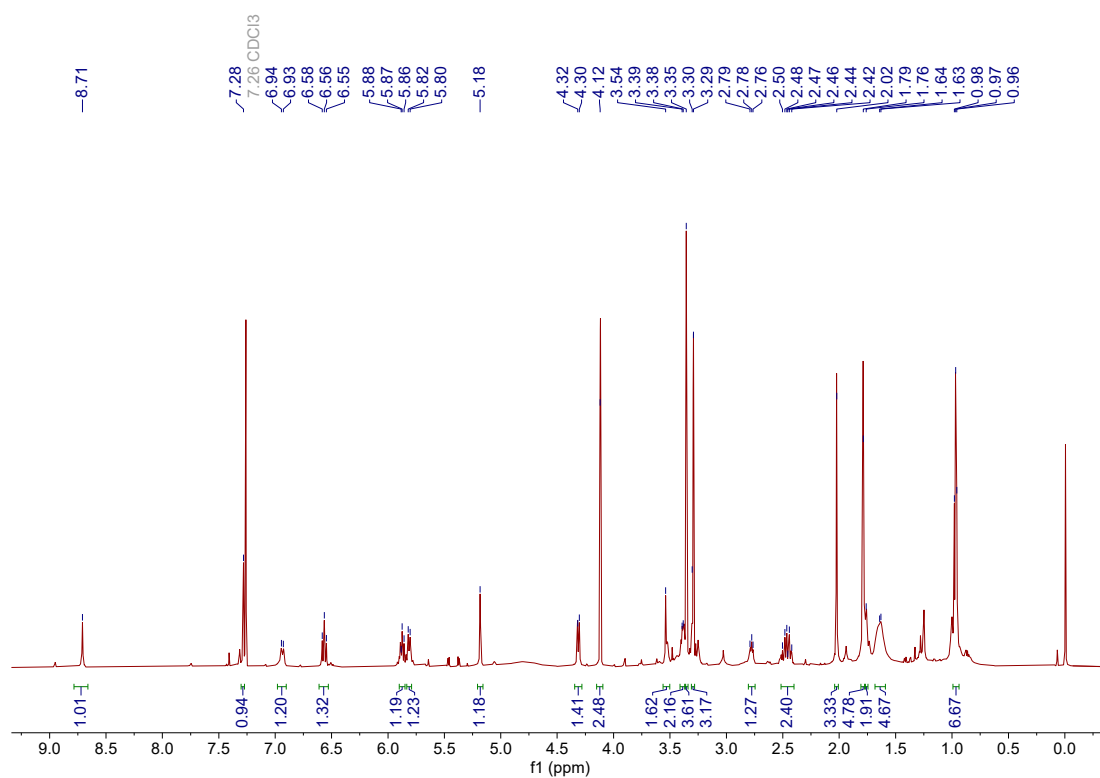
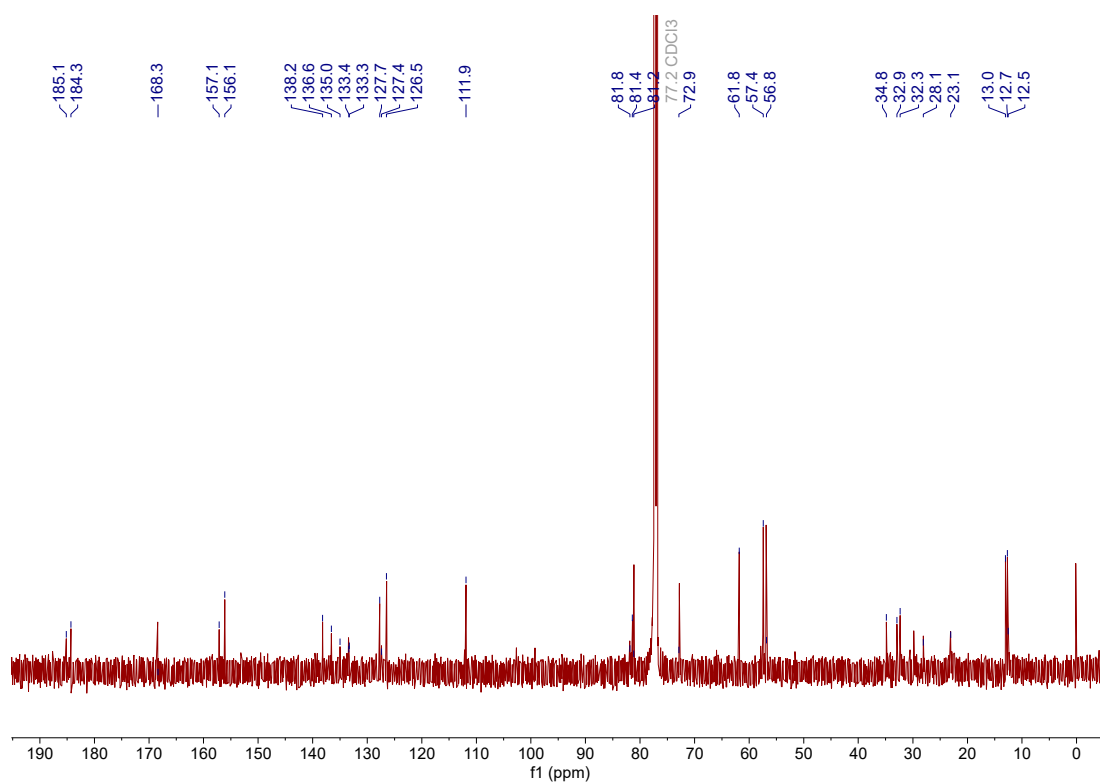
Formula (M)	Ion Formula	m/z	Calc m/z	Diff (ppm)	DBE
C ₁₁ H ₂₀ O ₄	C ₁₁ H ₂₀ NaO ₄	239.1249	239.1254	-2.0	2

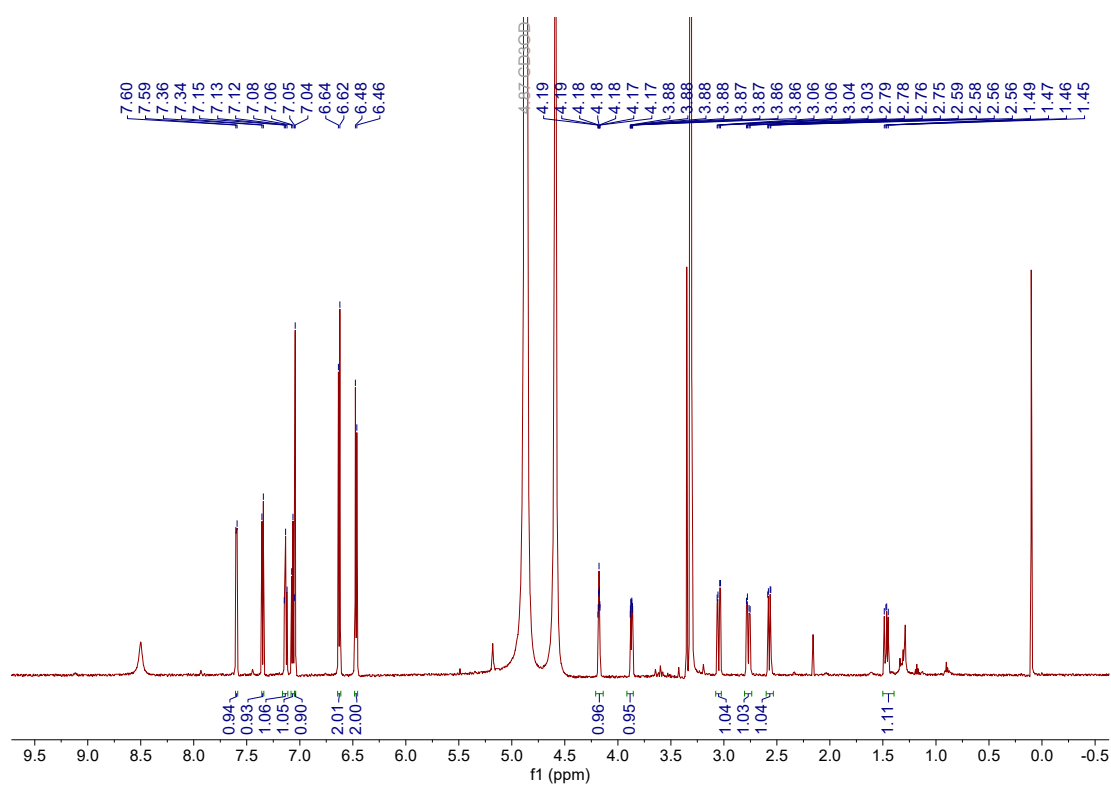
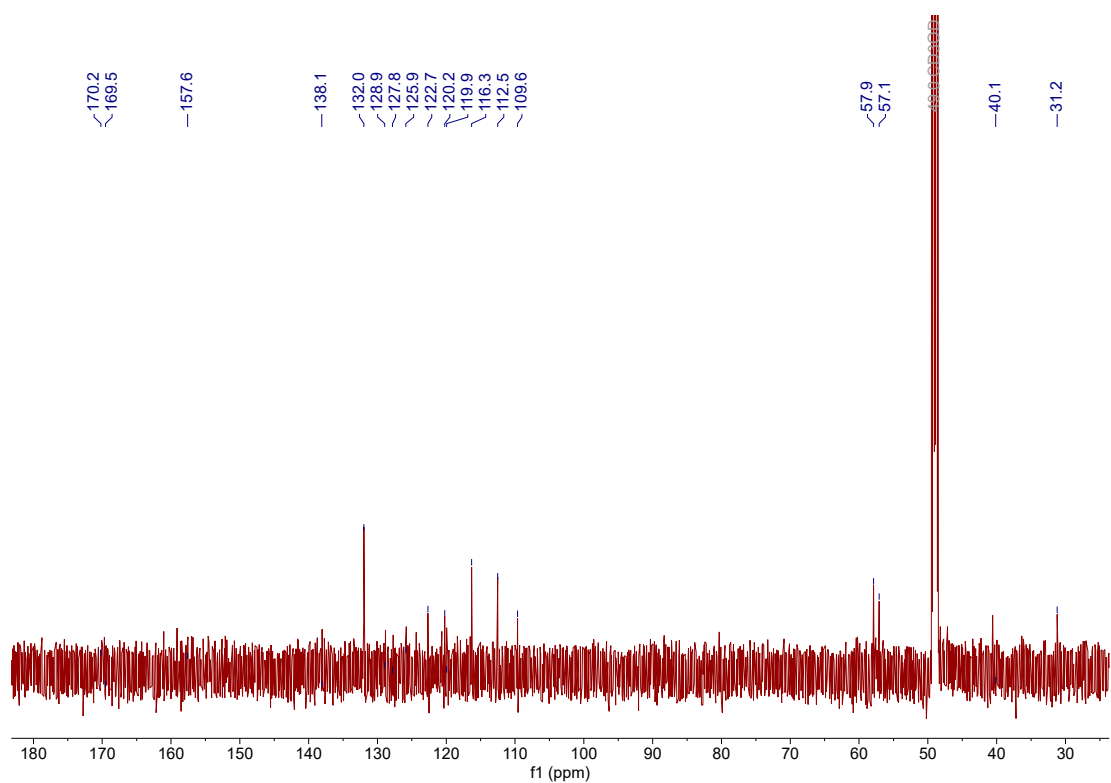
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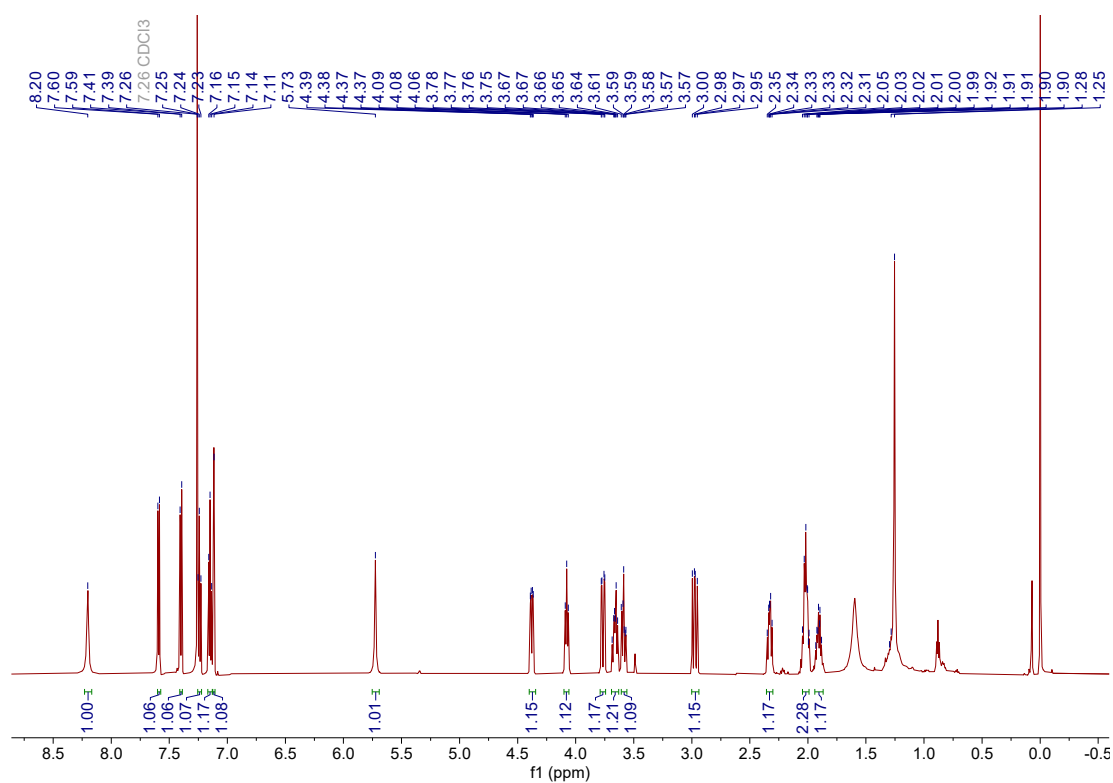
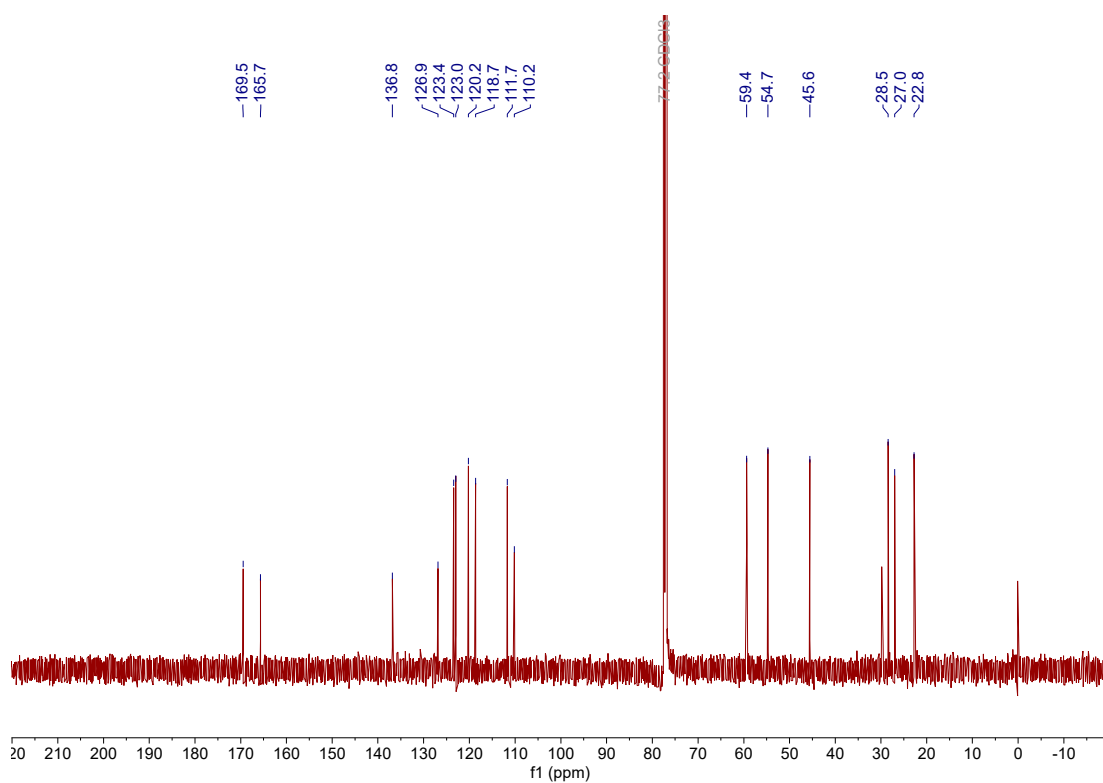
Figure S3a. ¹H NMR spectrum of 3 in DMSO.Figure S3b. ¹³C NMR spectrum of 3 in DMSO.

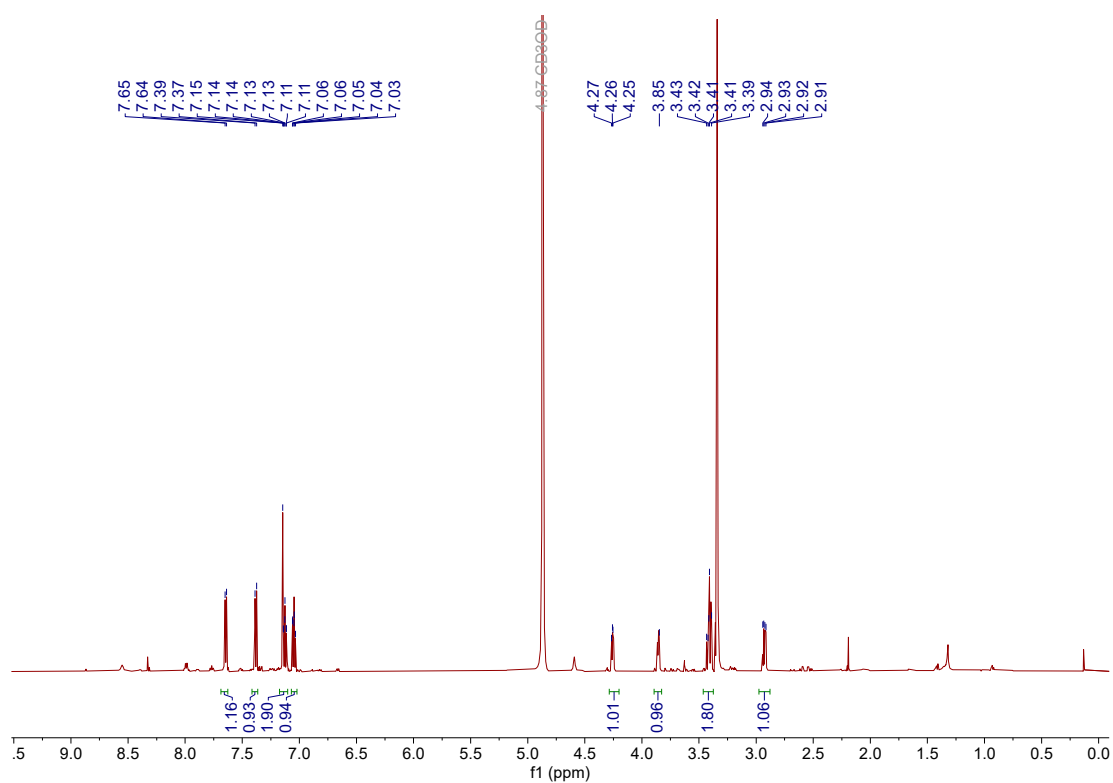
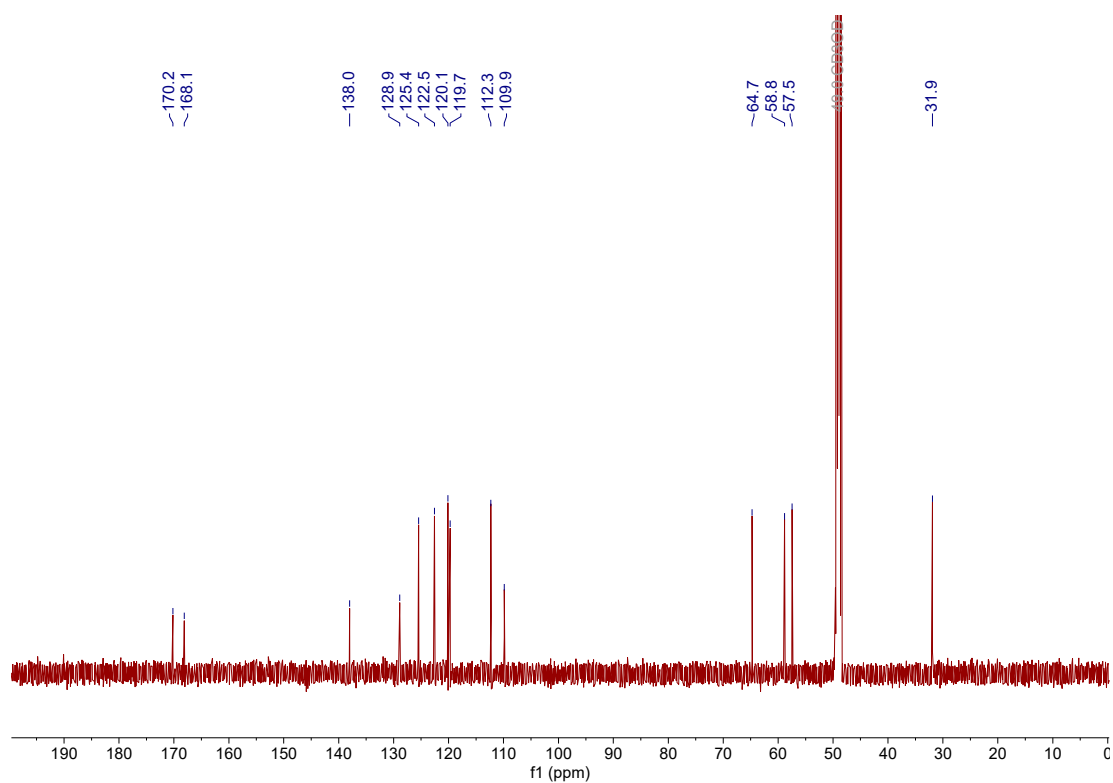
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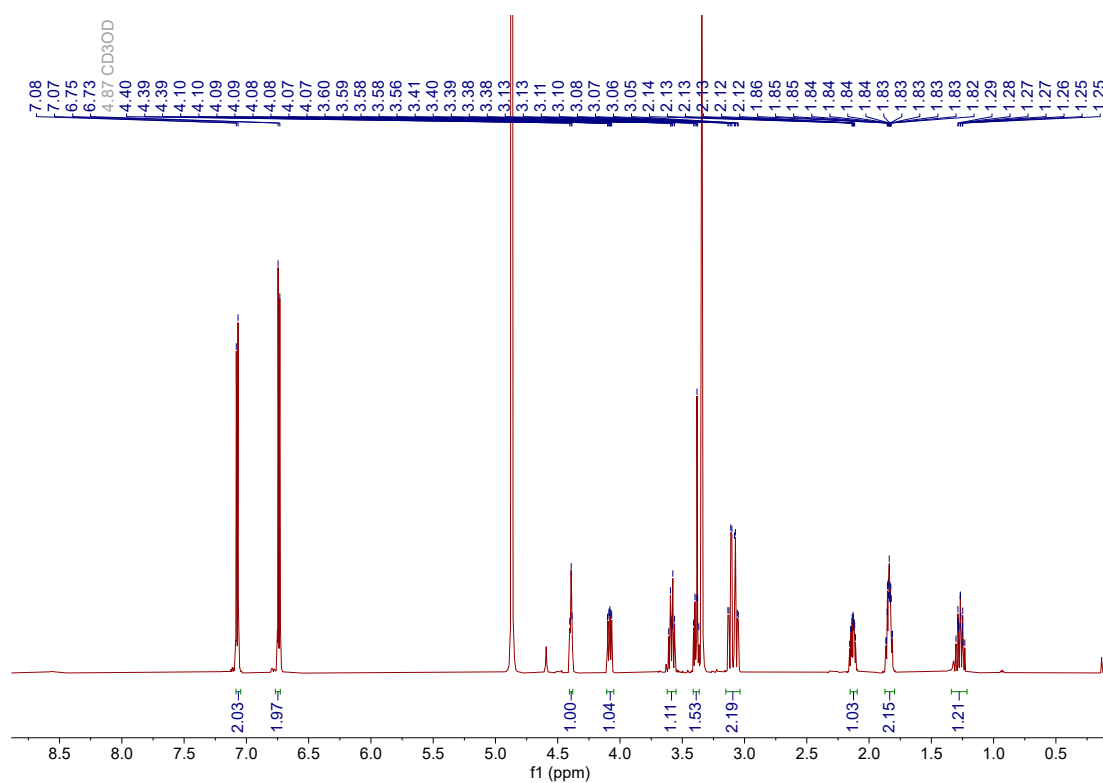
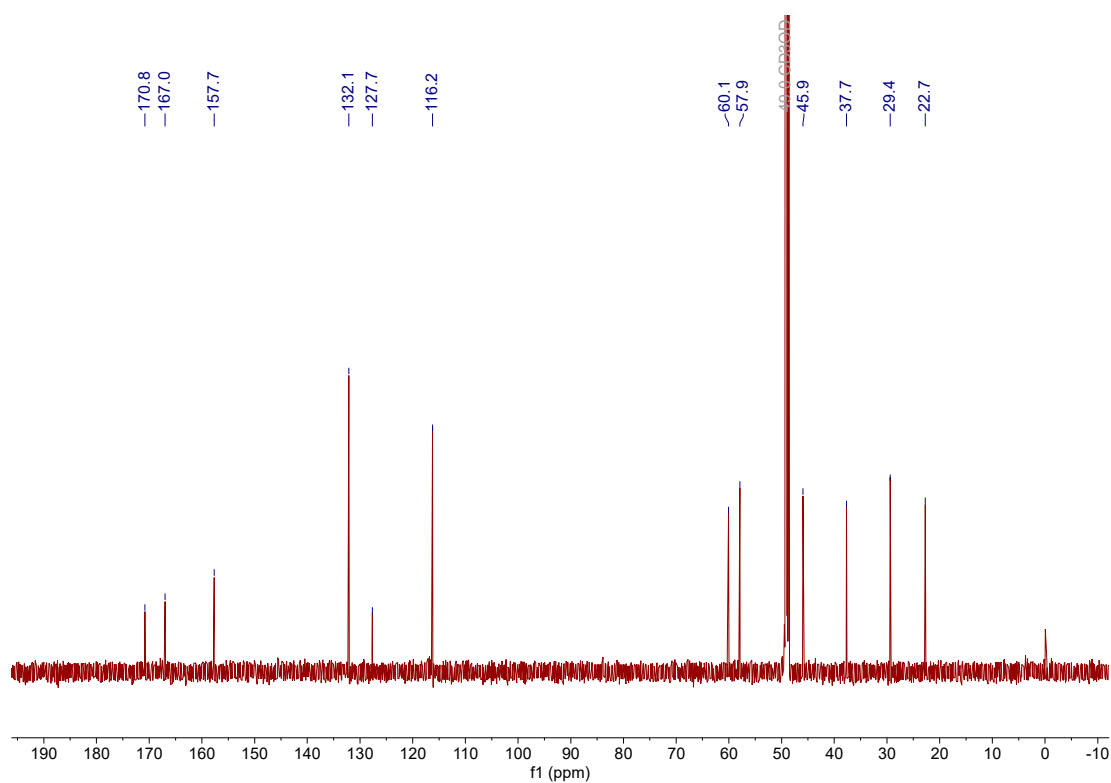
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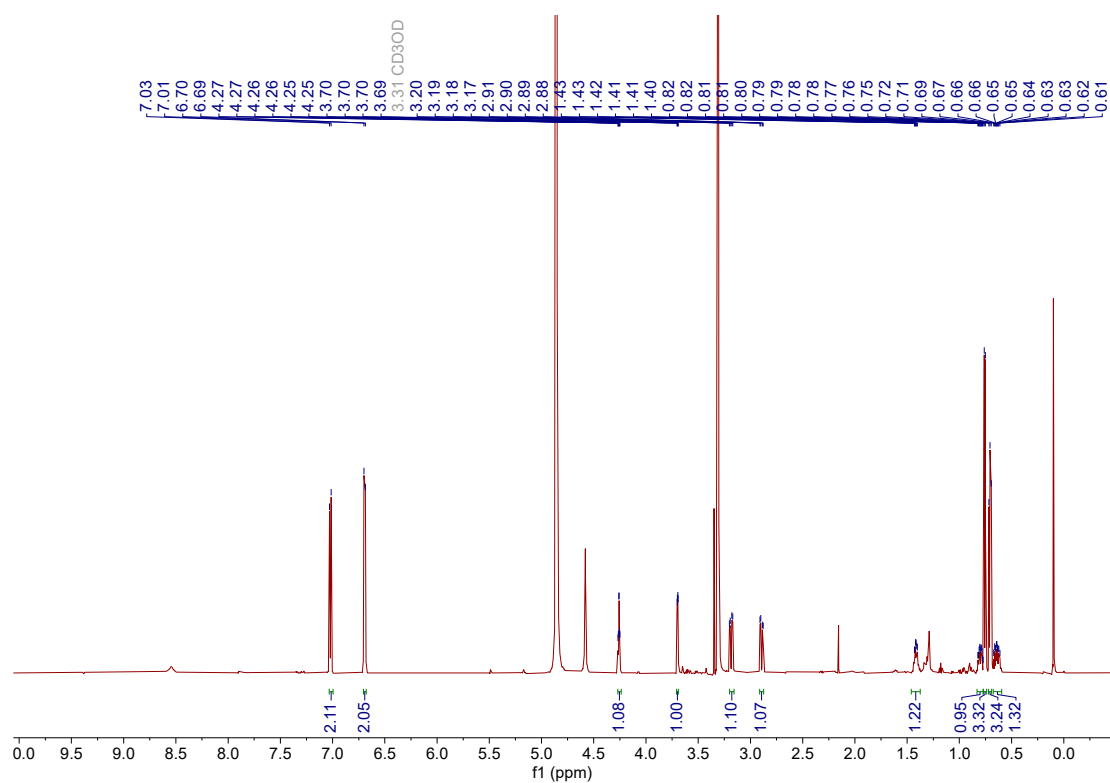
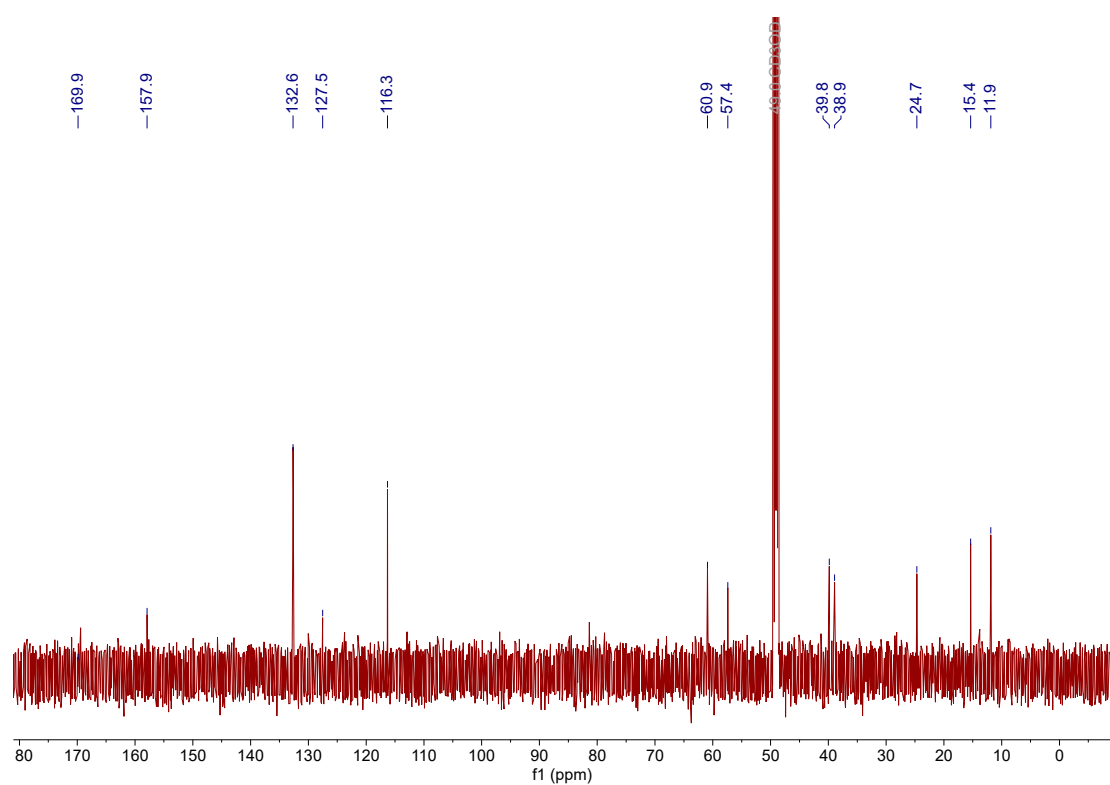
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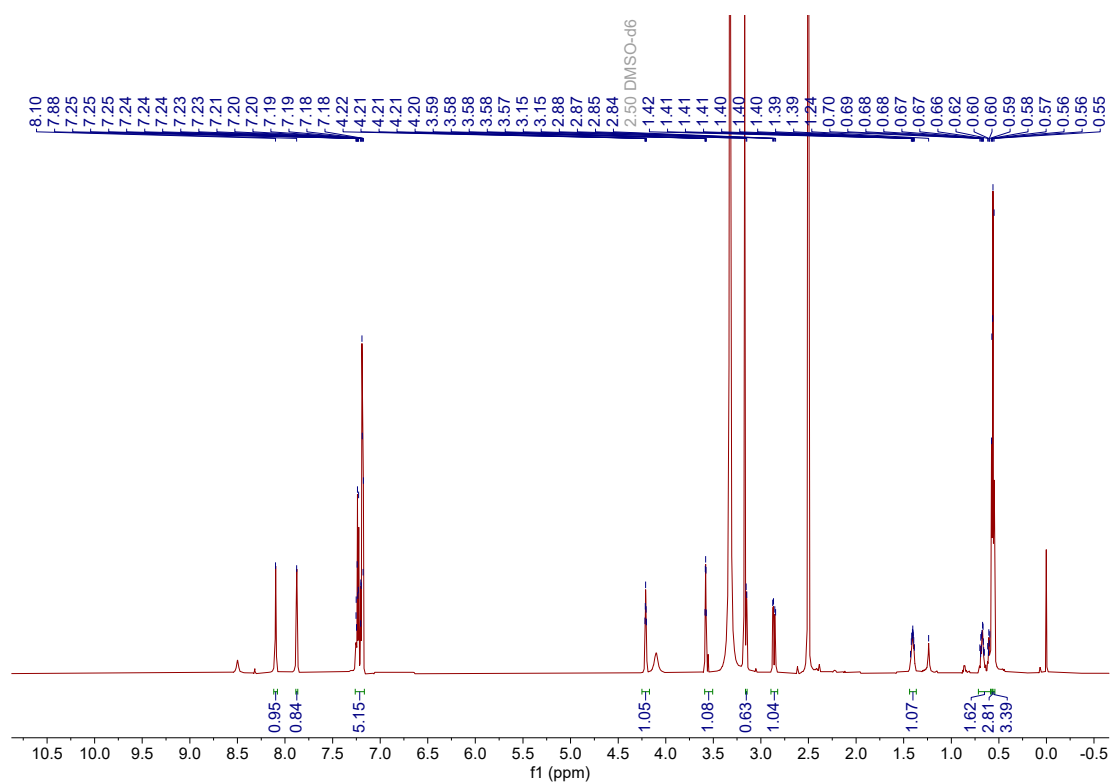
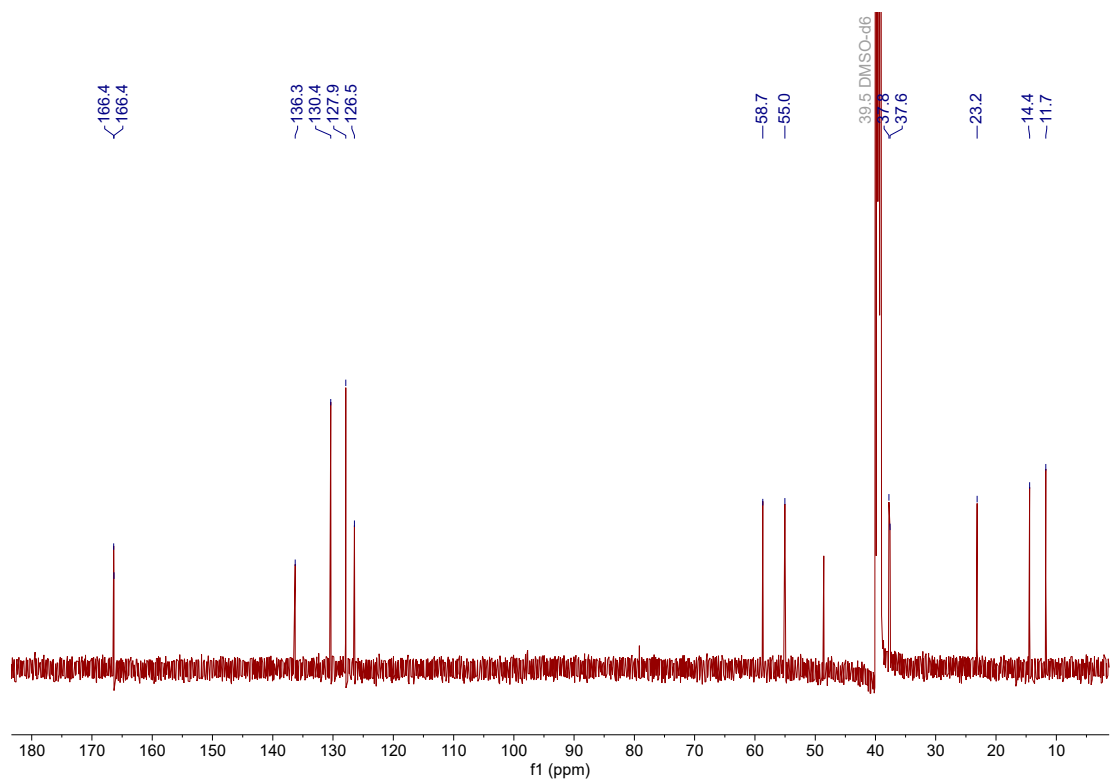
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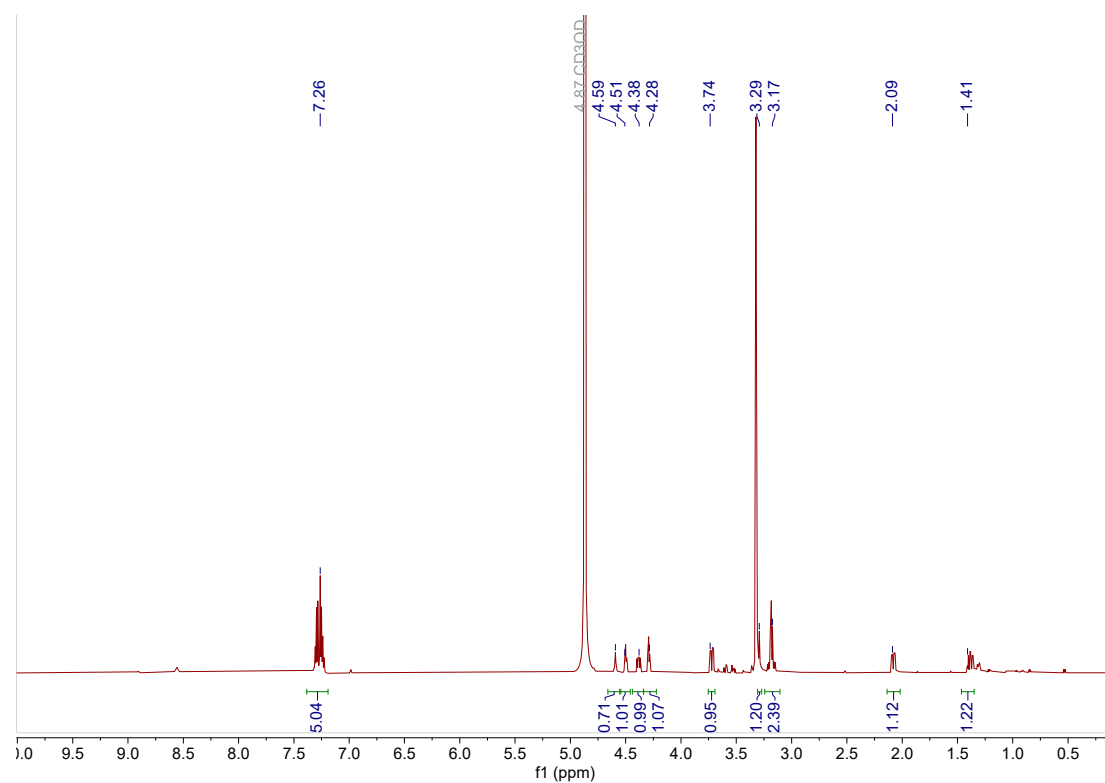
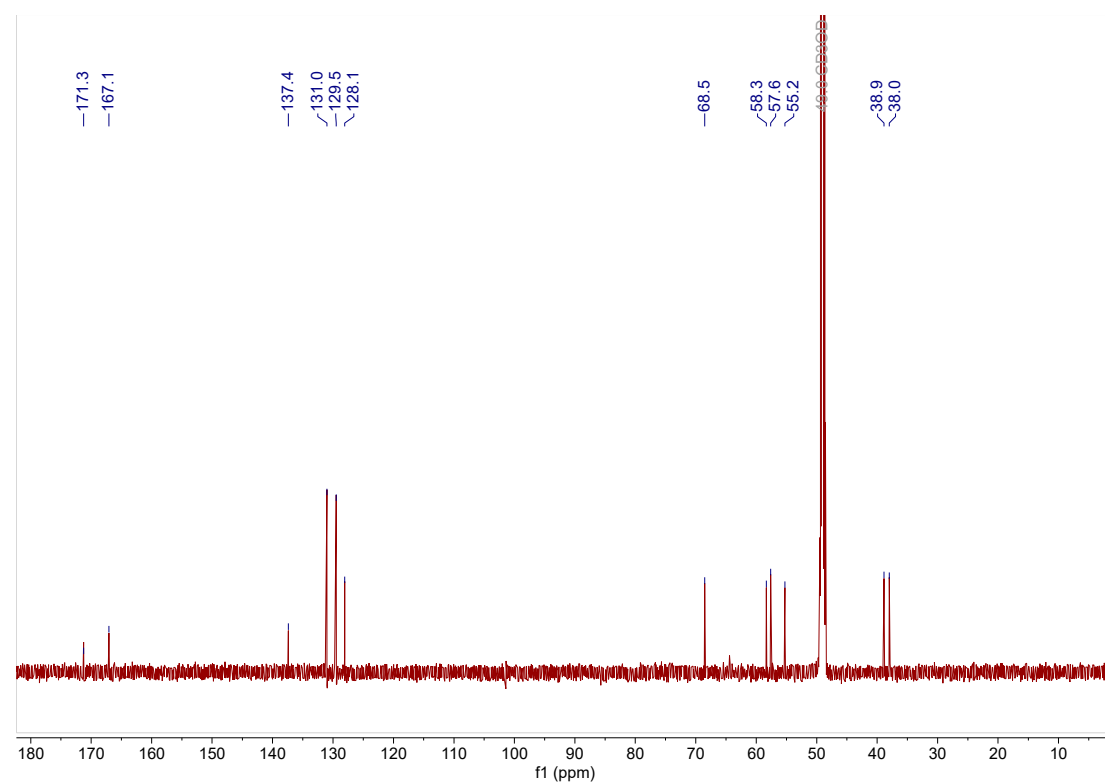
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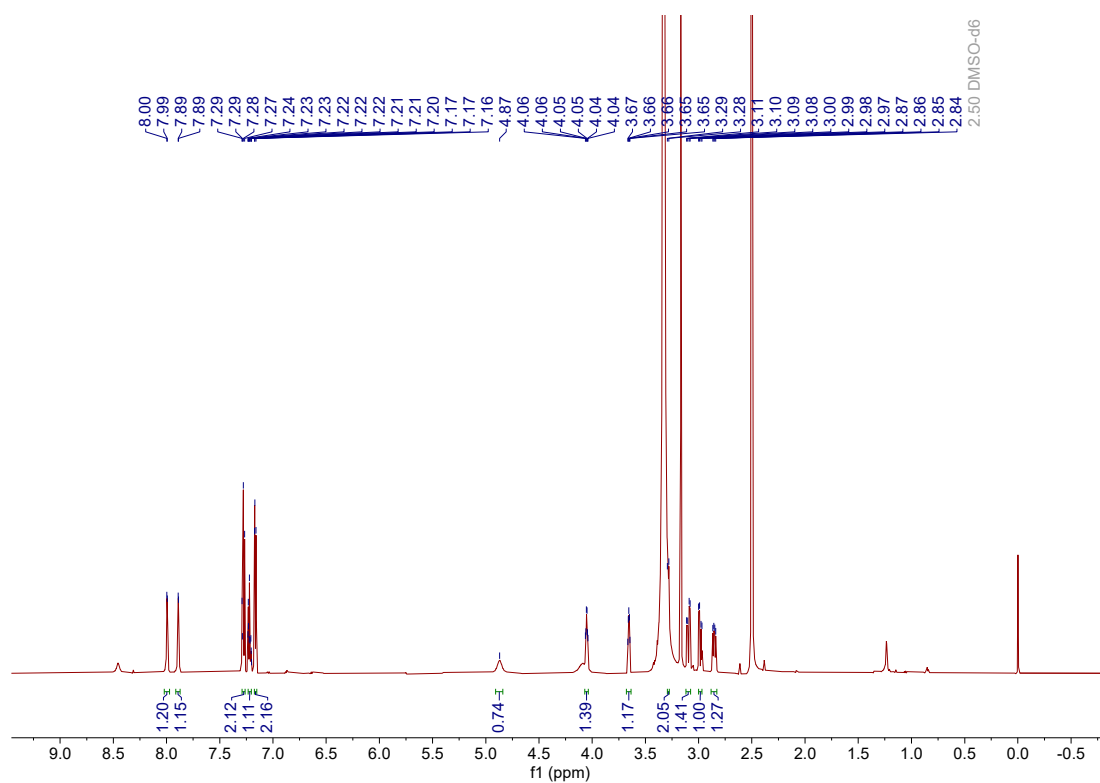
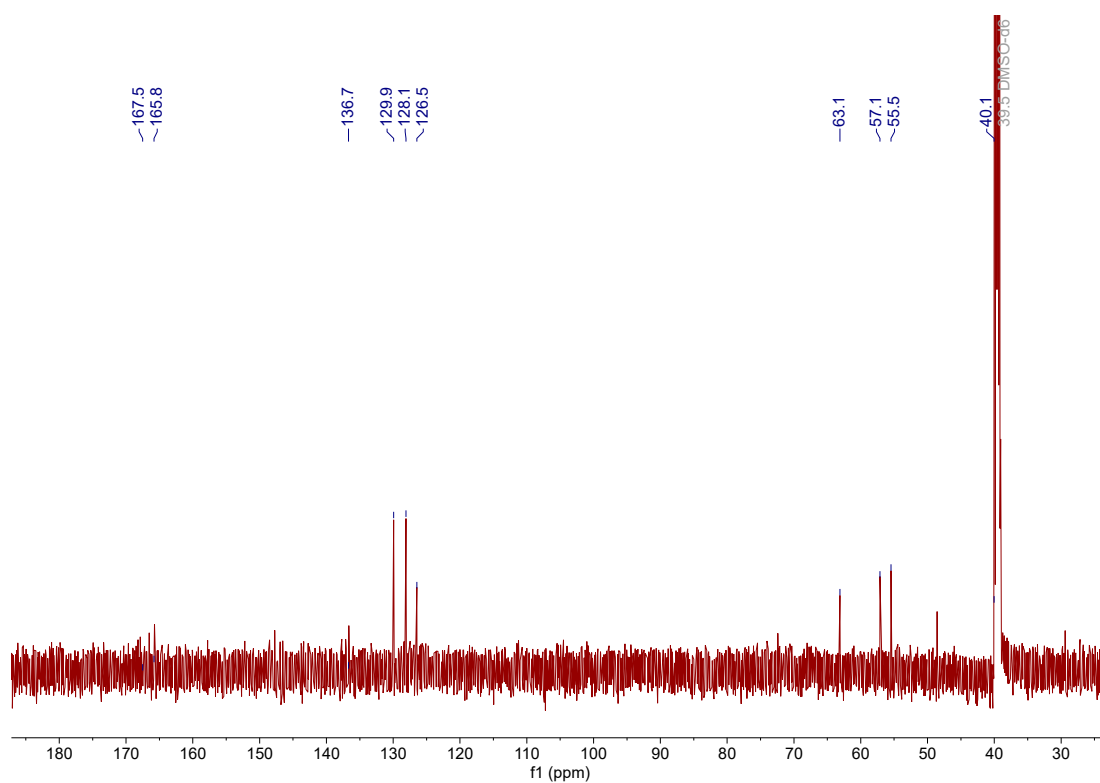
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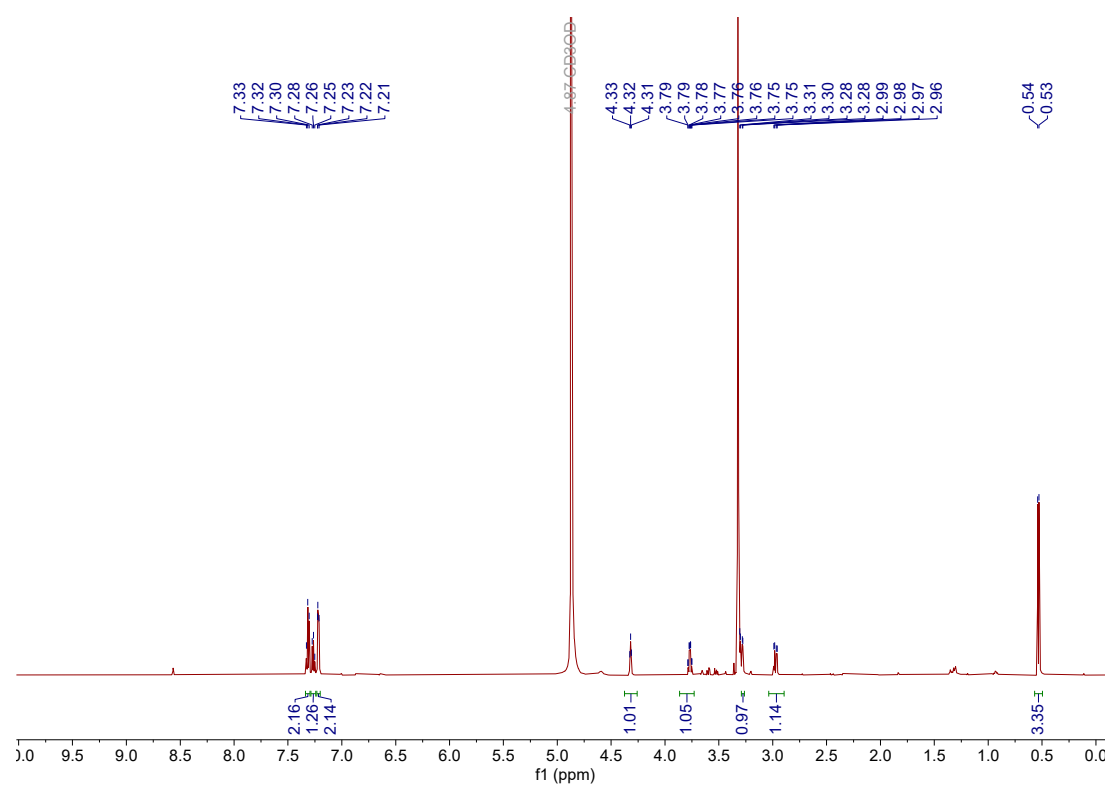
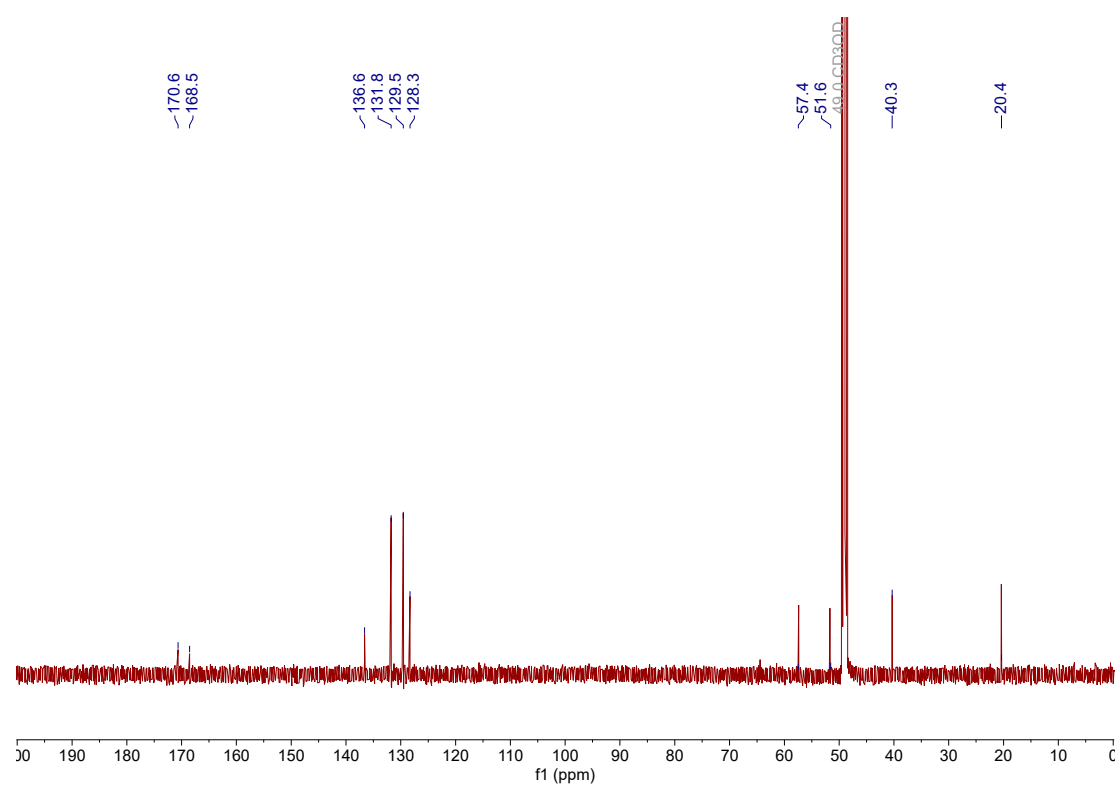
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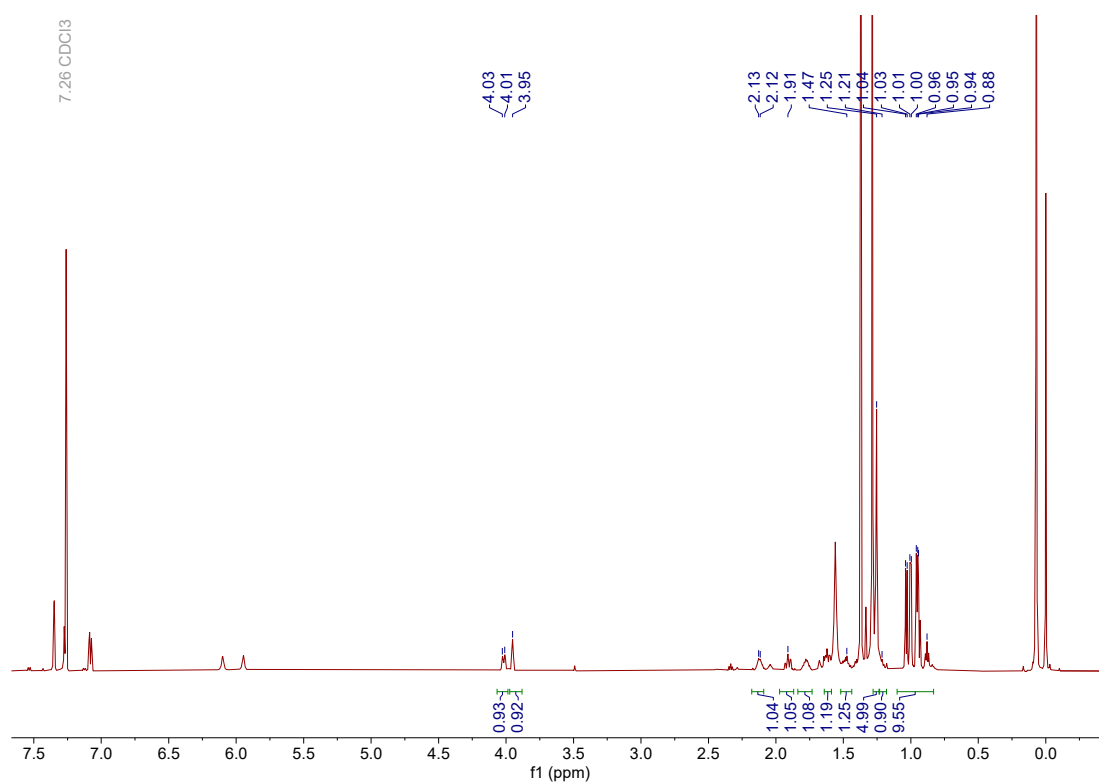
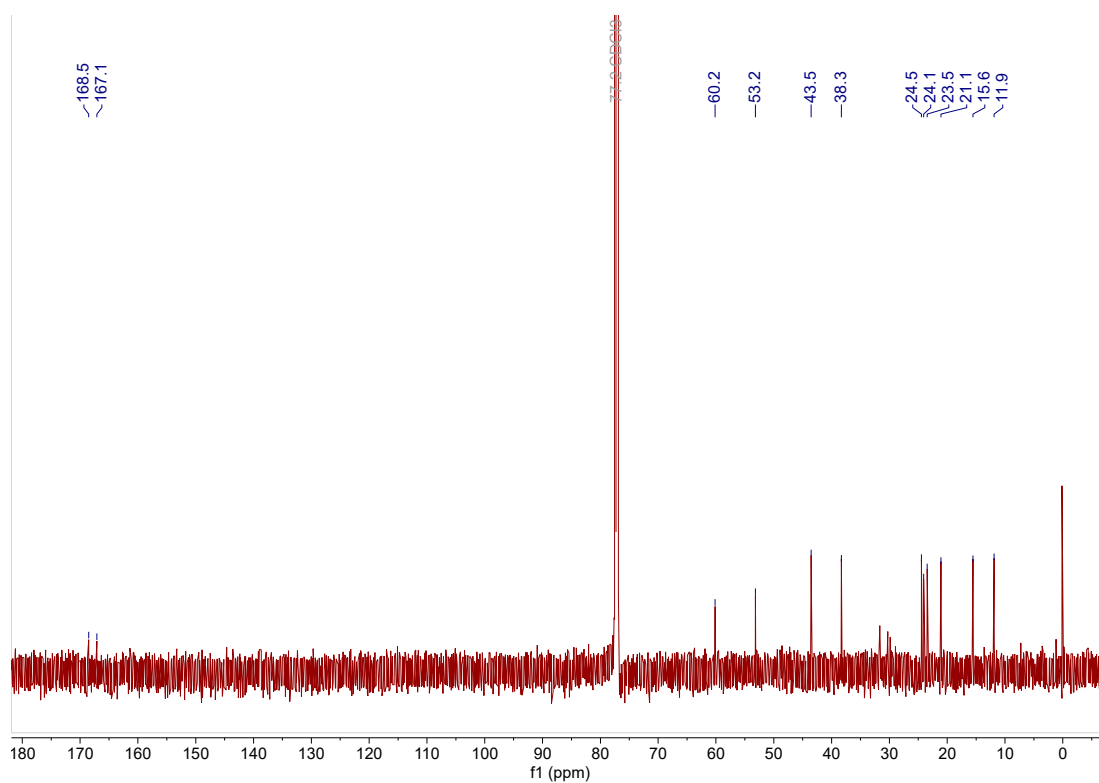
Figure S11a. ¹H NMR spectrum of 11 in CD₃OD.Figure S11b. ¹³C NMR spectrum of 11 in CD₃OD.

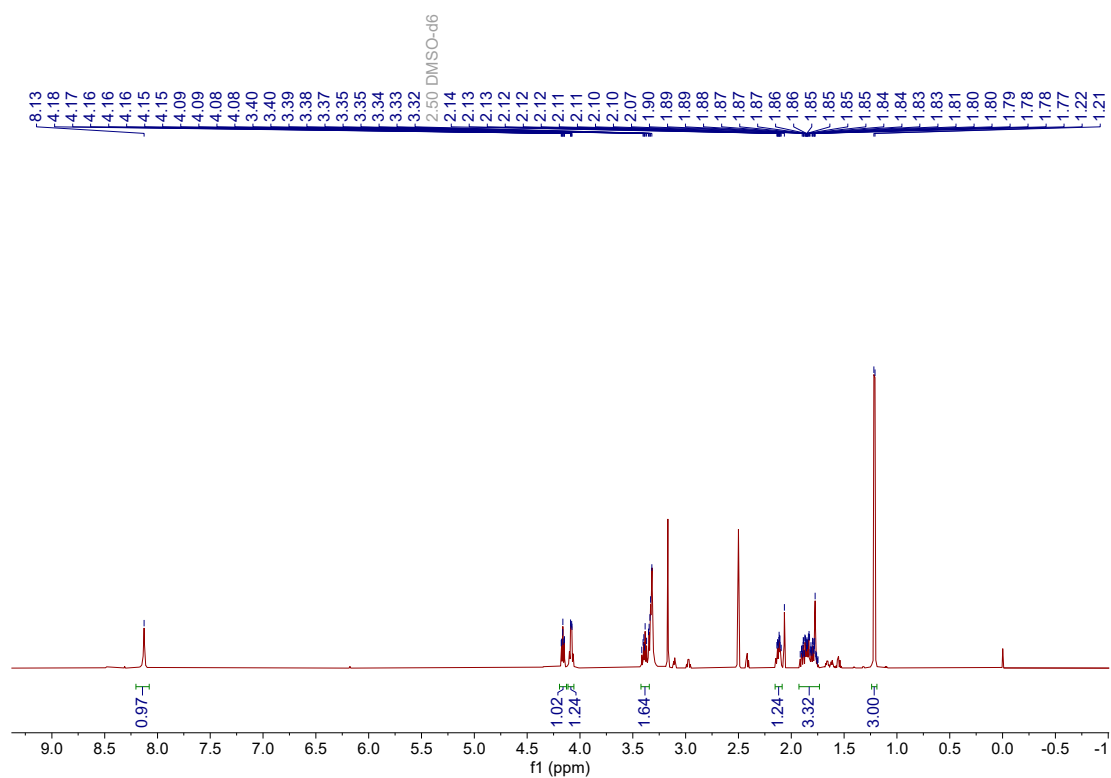
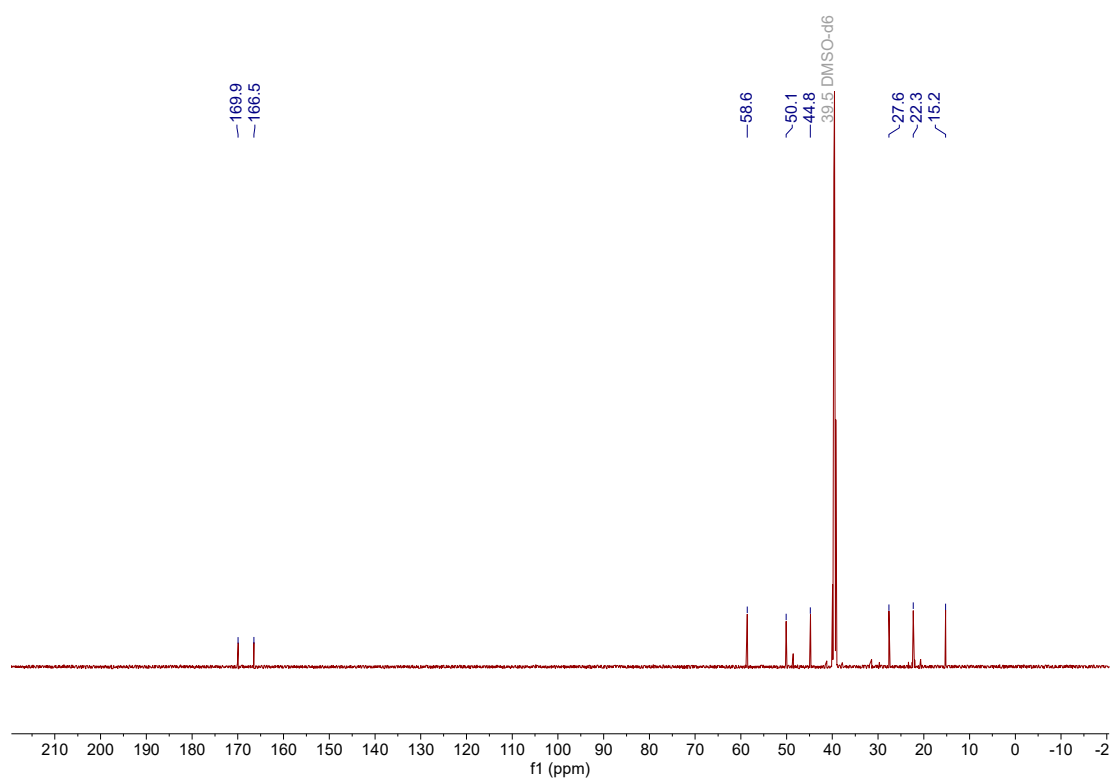
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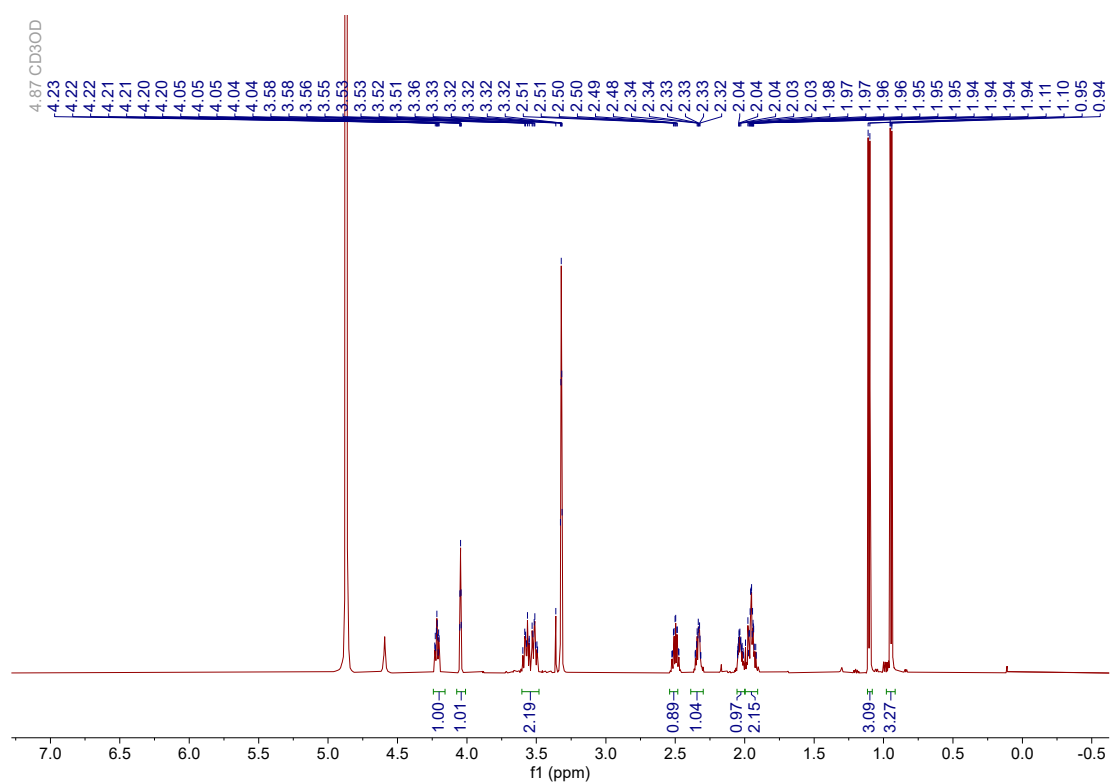
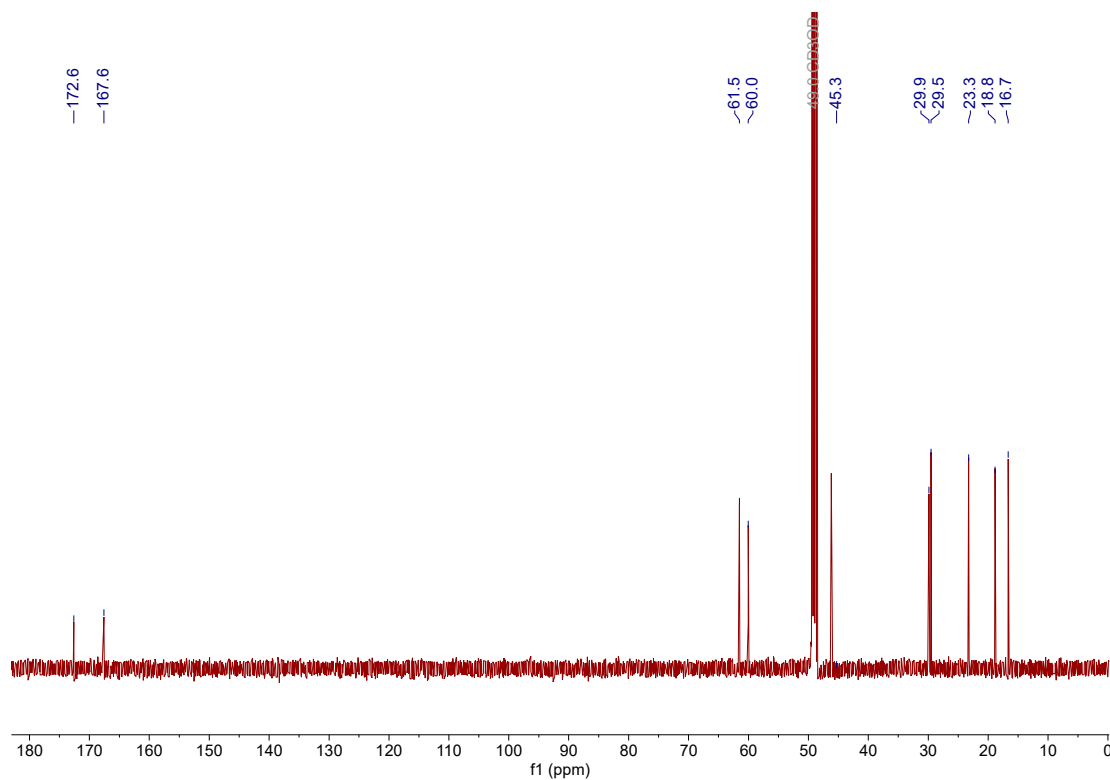
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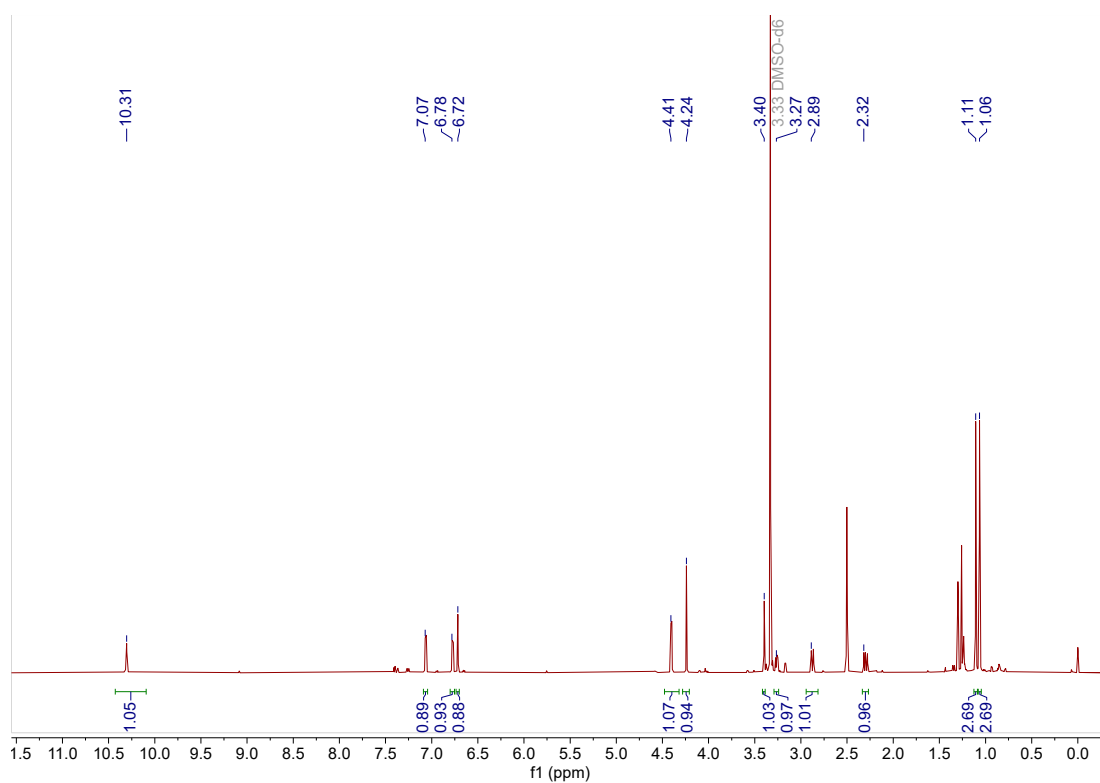
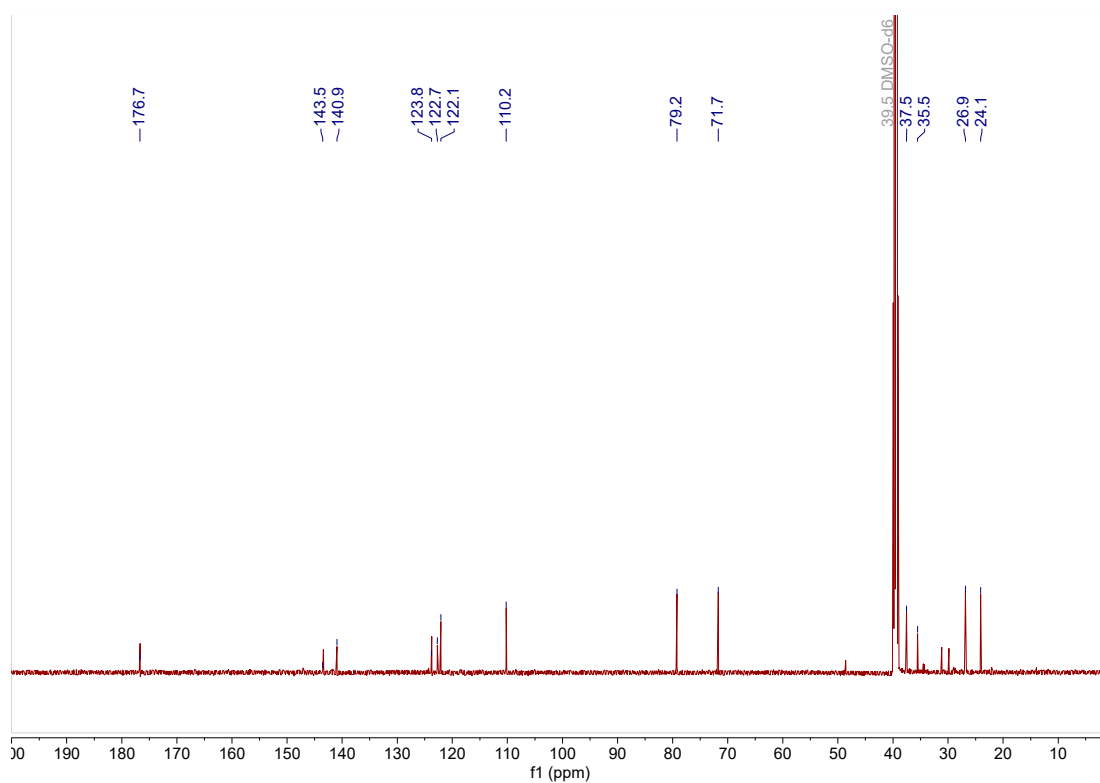
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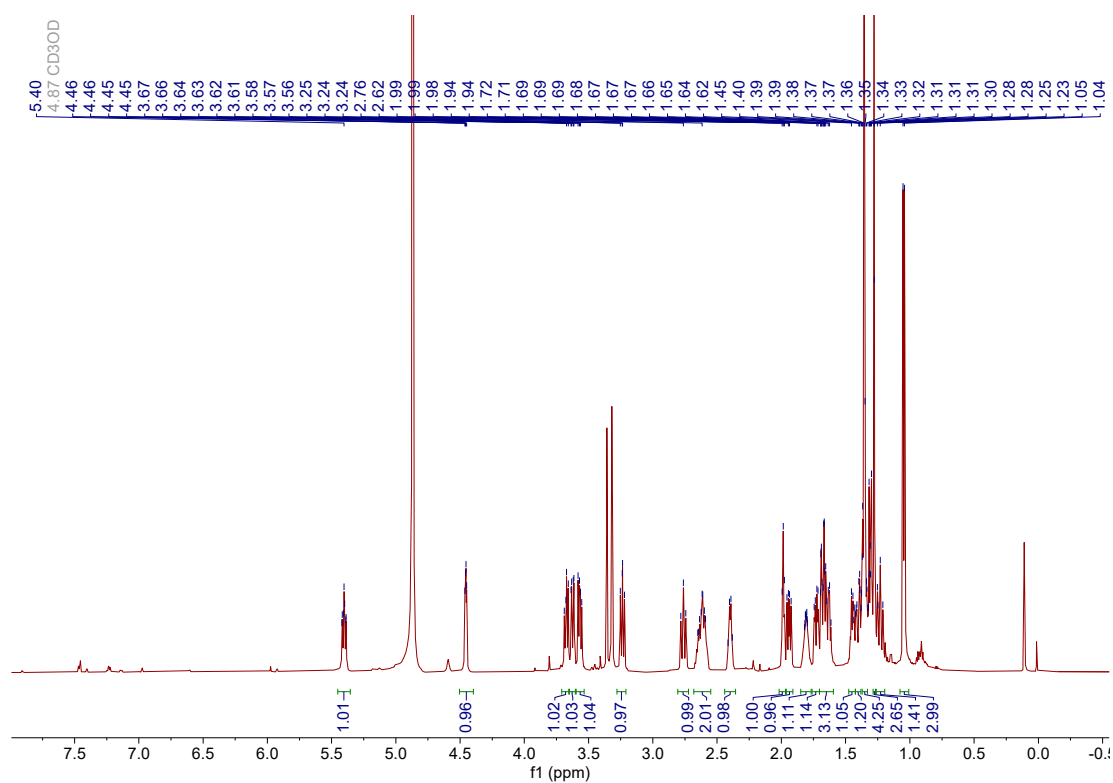
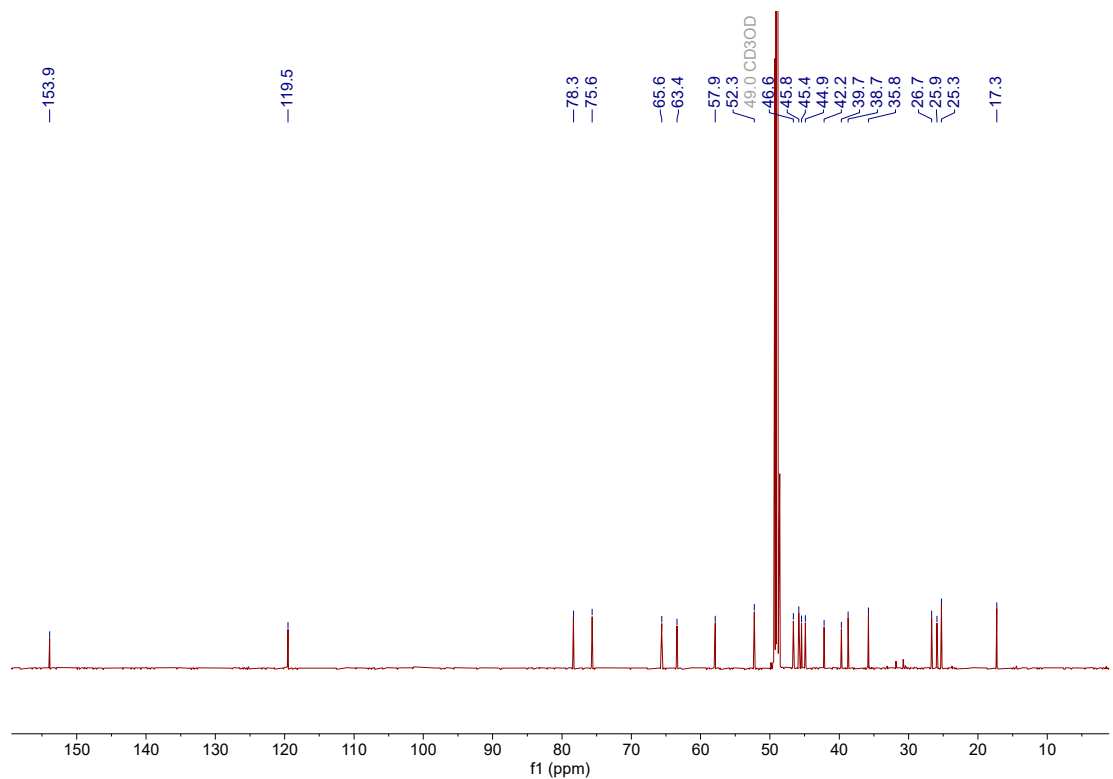
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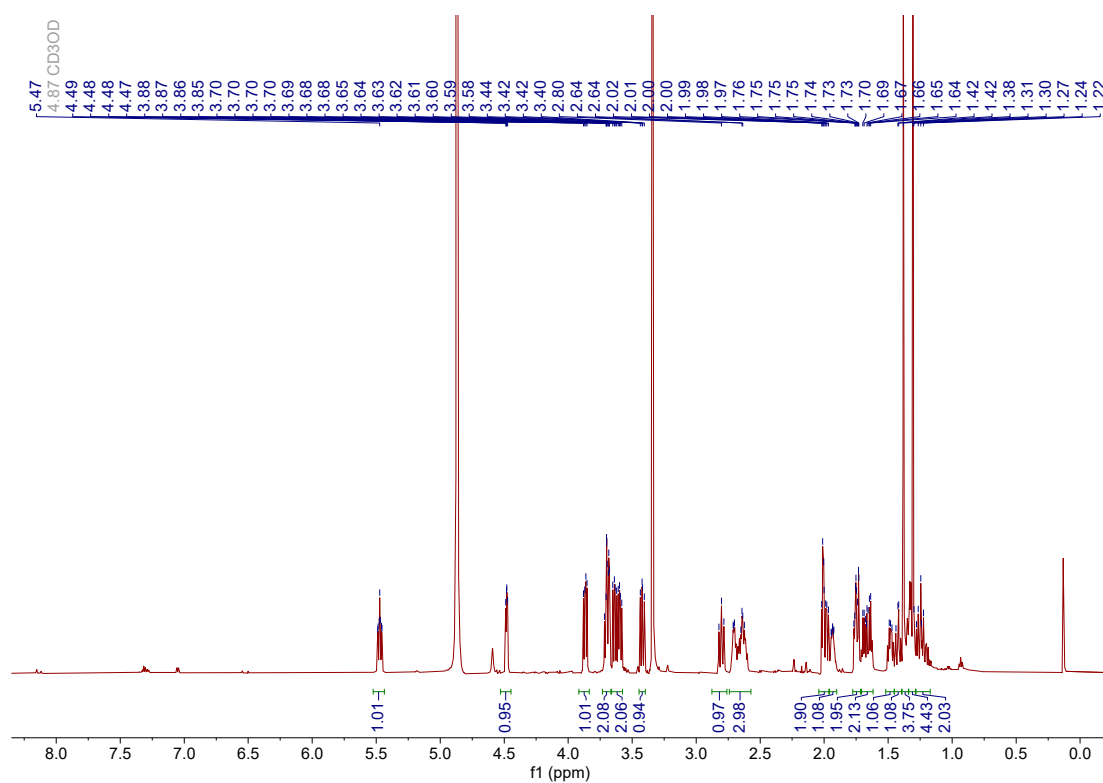
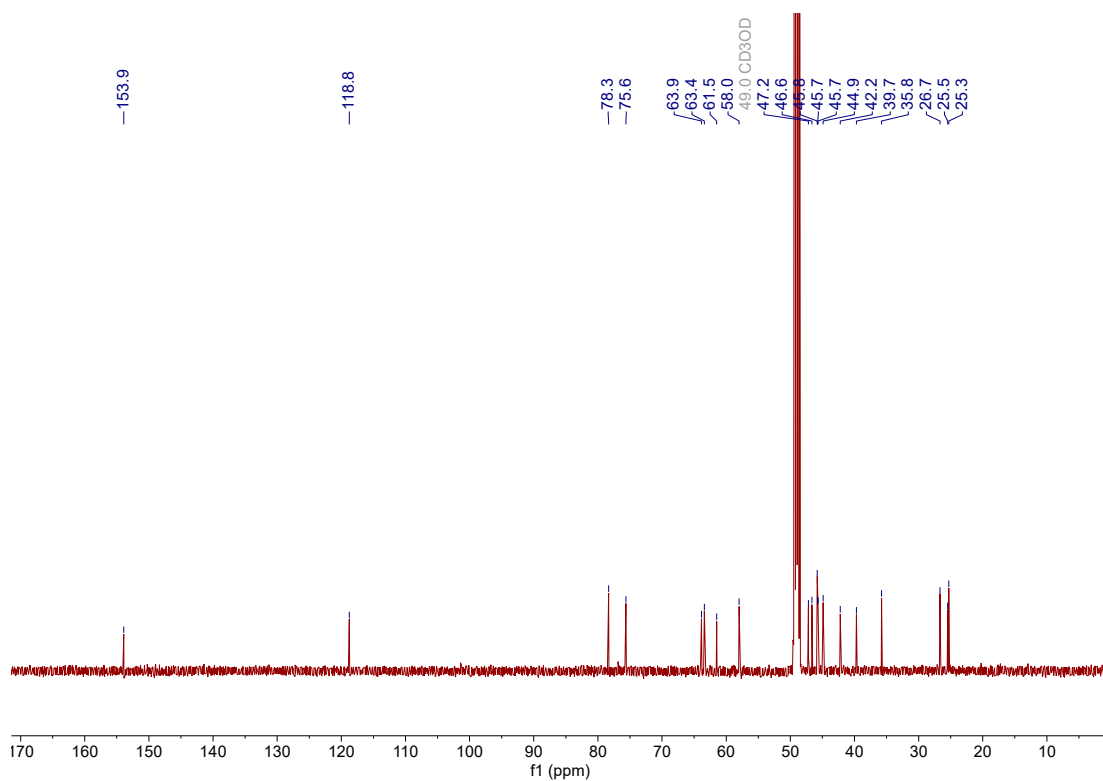
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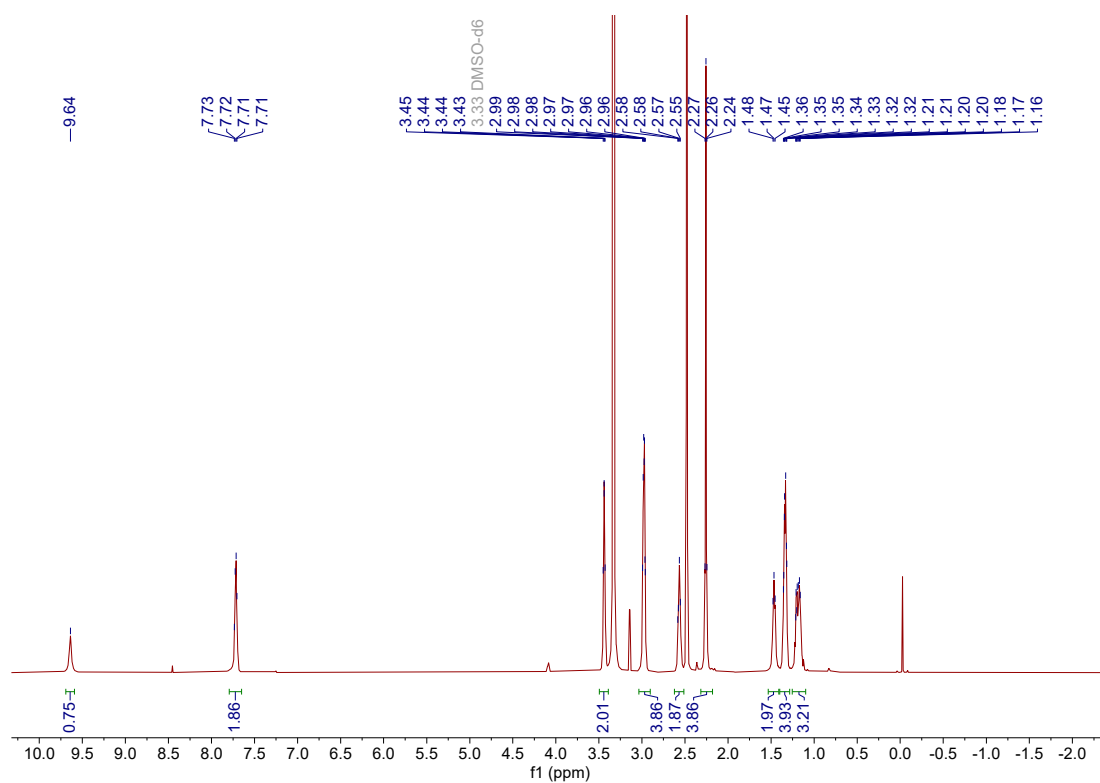
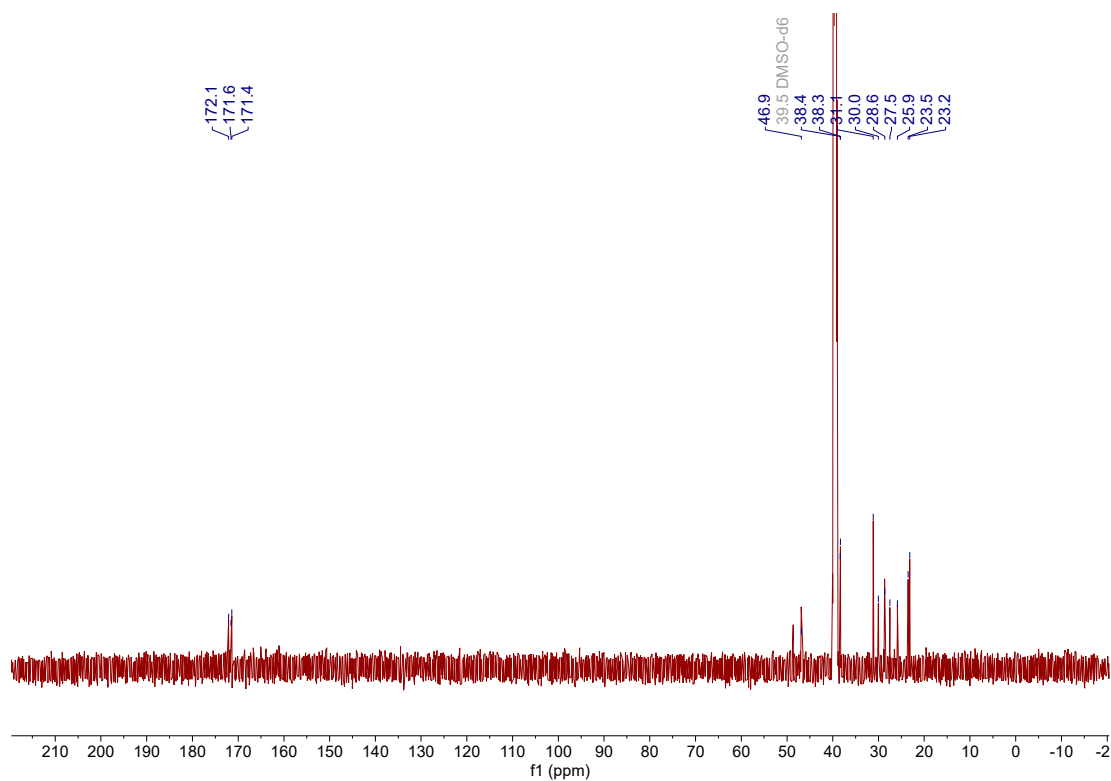
Figure S17a. ¹H NMR spectrum of 17 in DMSO.Figure S17b. ¹³C NMR spectrum of 17 in DMSO.

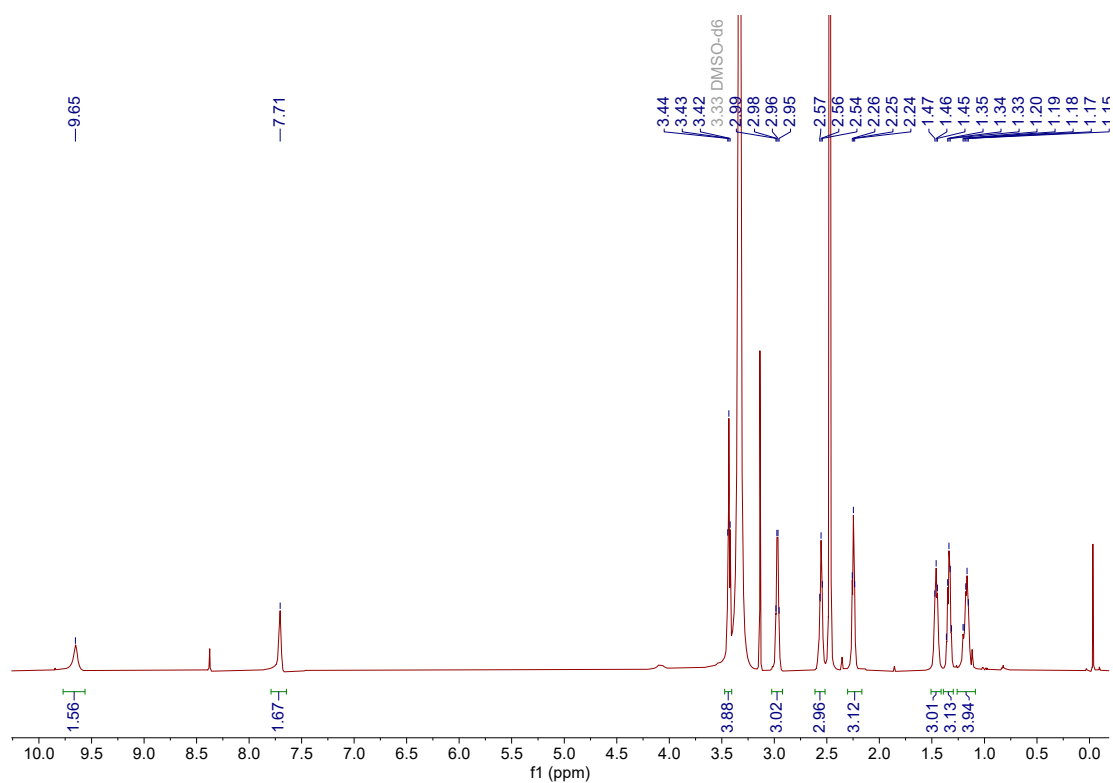
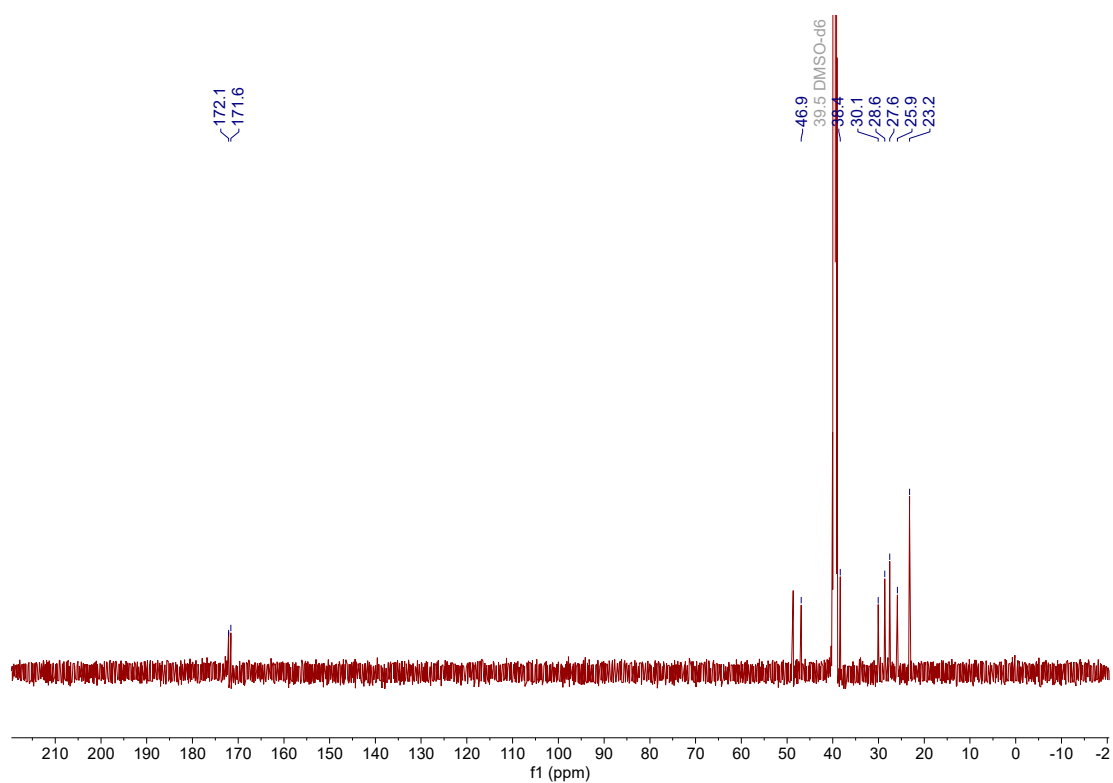
Figure S18a. ¹H NMR spectrum of 18 in CD₃OD.Figure S18b. ¹³C NMR spectrum of 18 in CD₃OD.

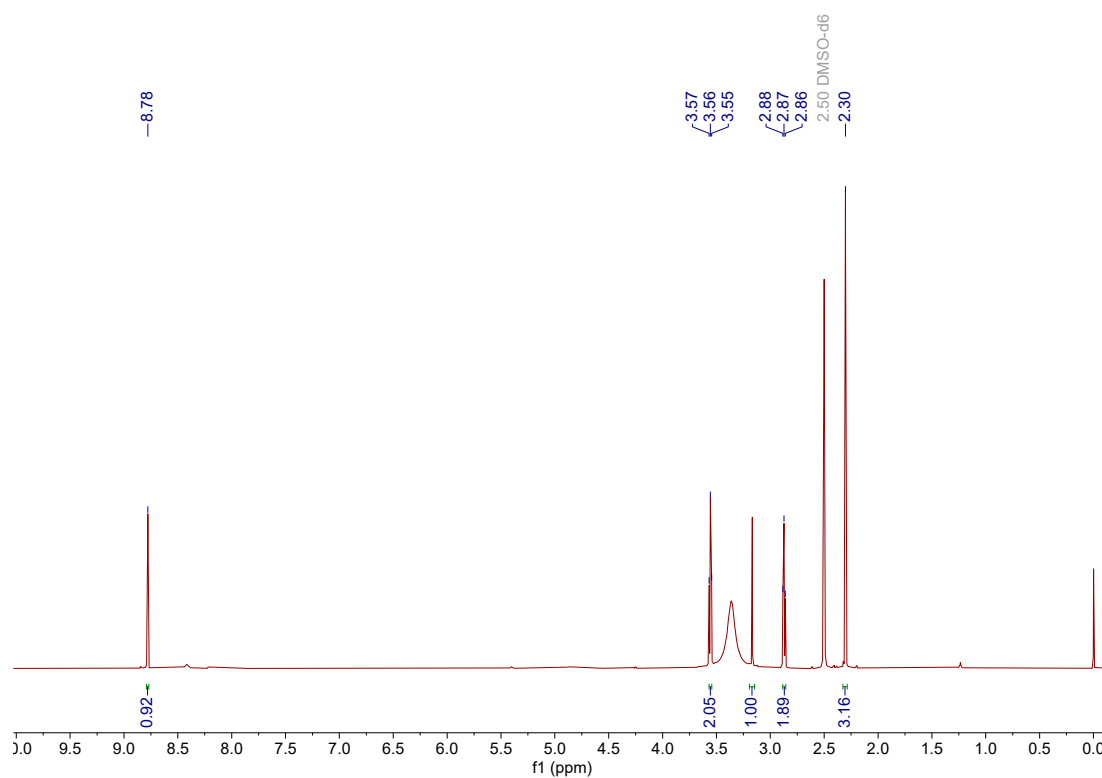
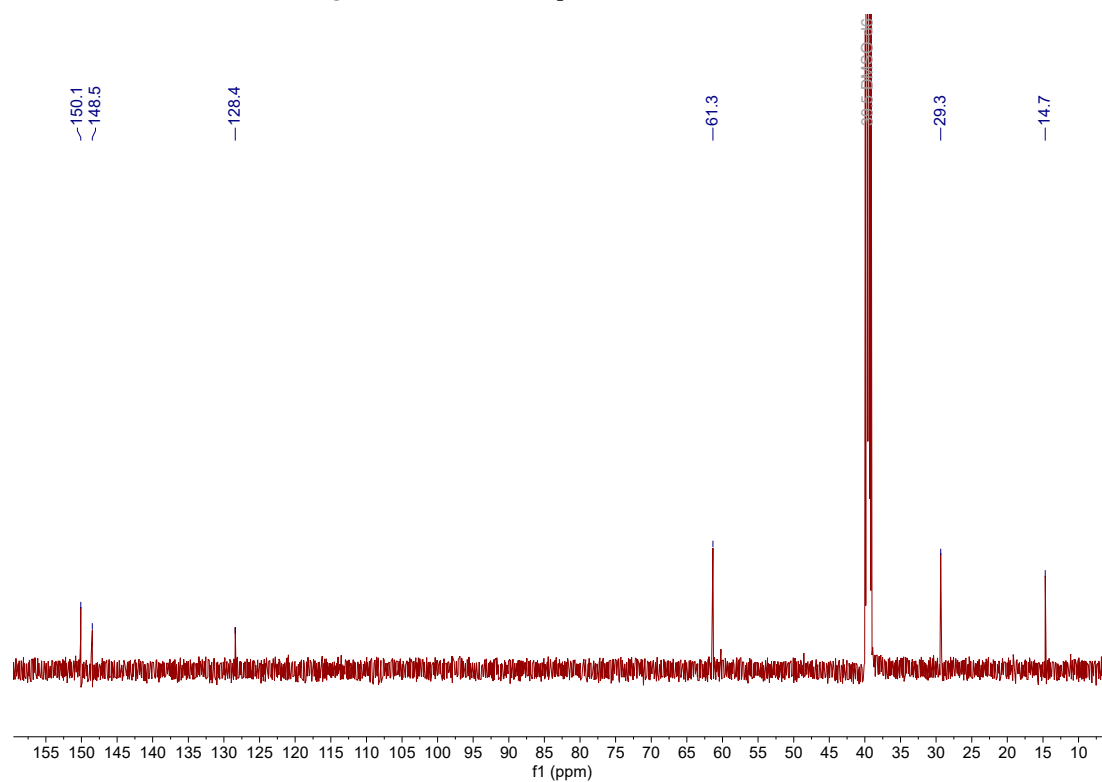
Figure S19a. ¹H NMR spectrum of **19** in DMSO.Figure S19b. ¹³C NMR spectrum of **19** in DMSO.

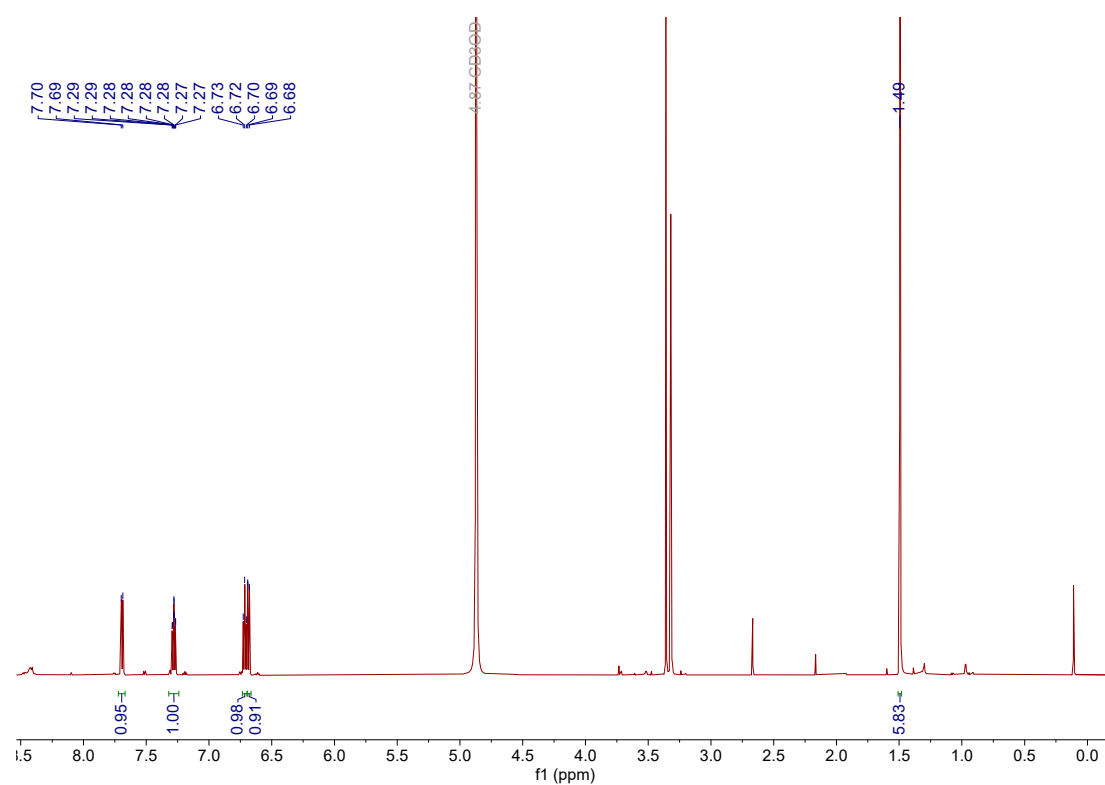
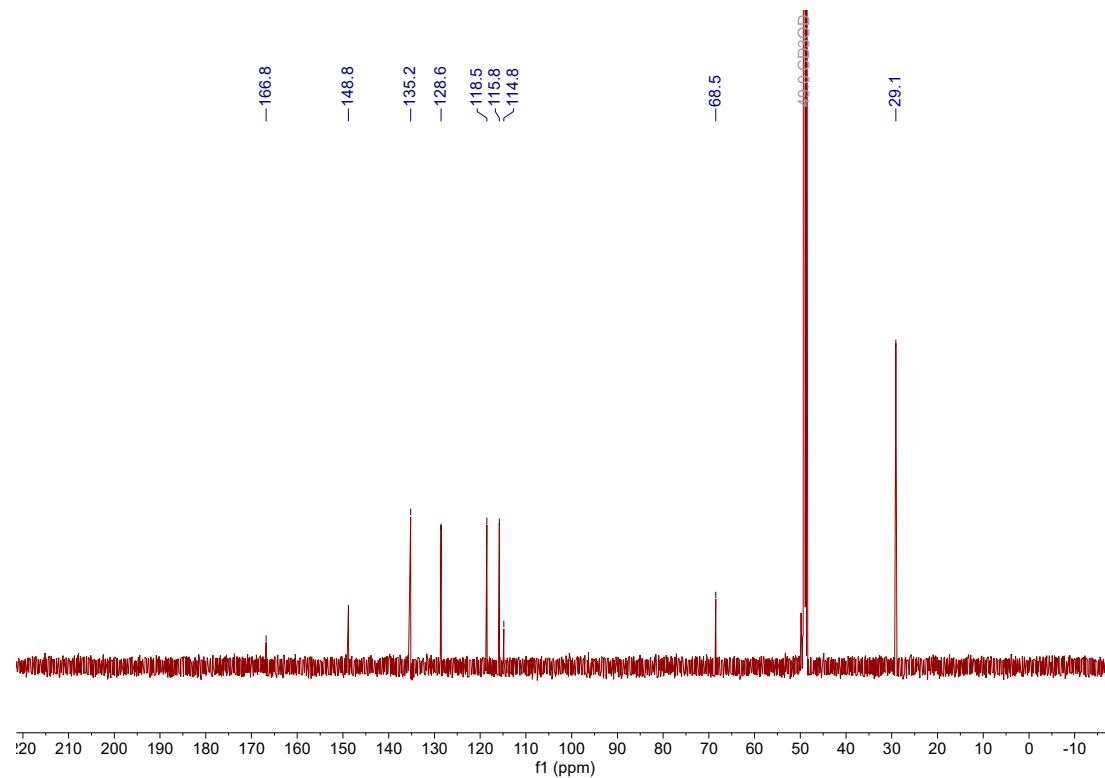
Figure S20a. ¹H NMR spectrum of 20 in CD₃OD.Figure S20b. ¹³C NMR spectrum of 20 in CD₃OD.

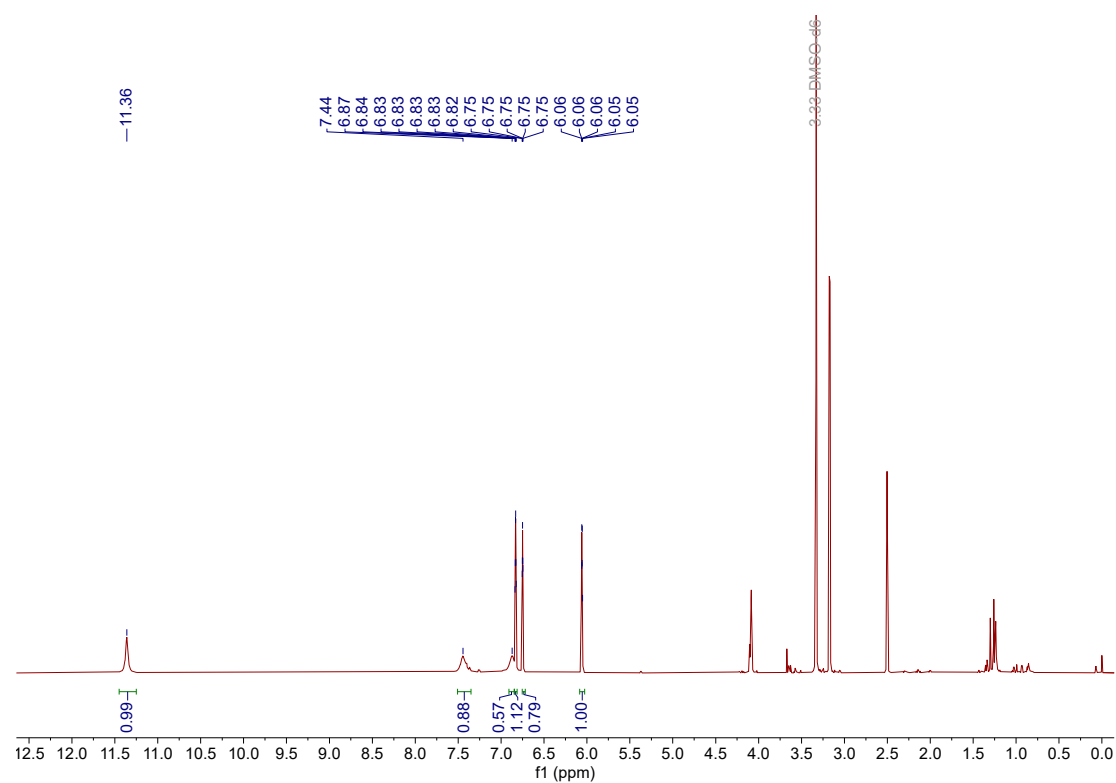
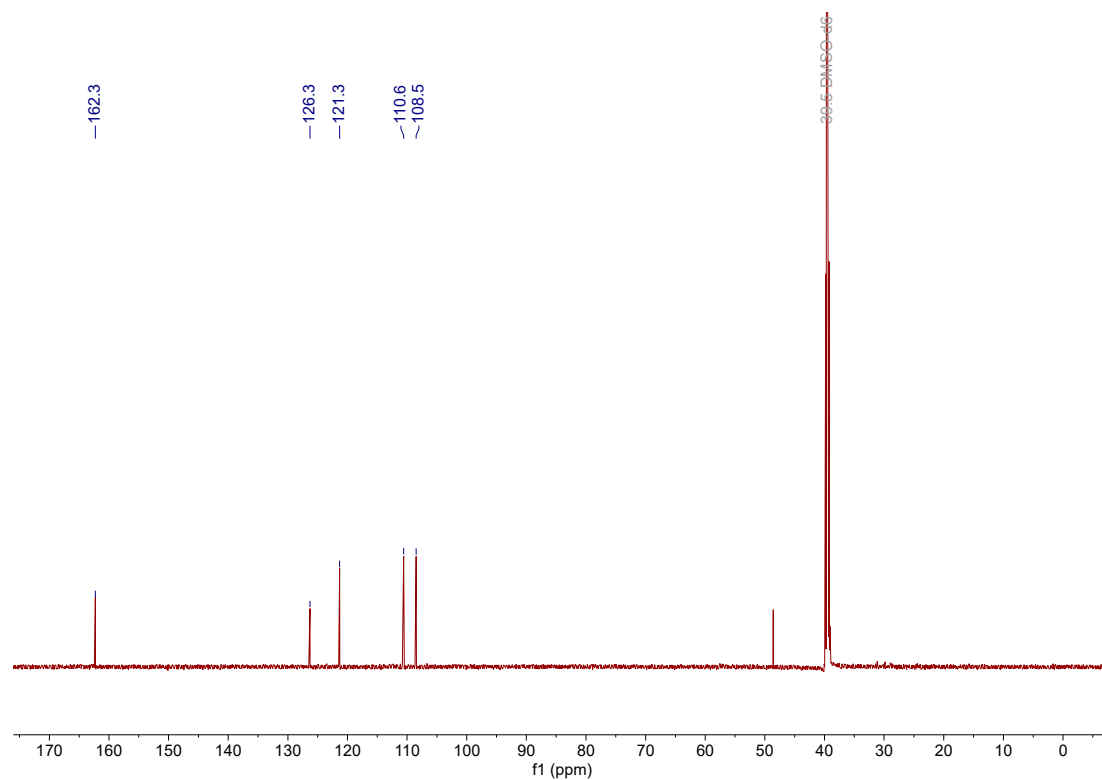
Figure S21a. ¹H NMR spectrum of 21 in CD₃OD.Figure S21b. ¹³C NMR spectrum of 21 in CD₃OD.

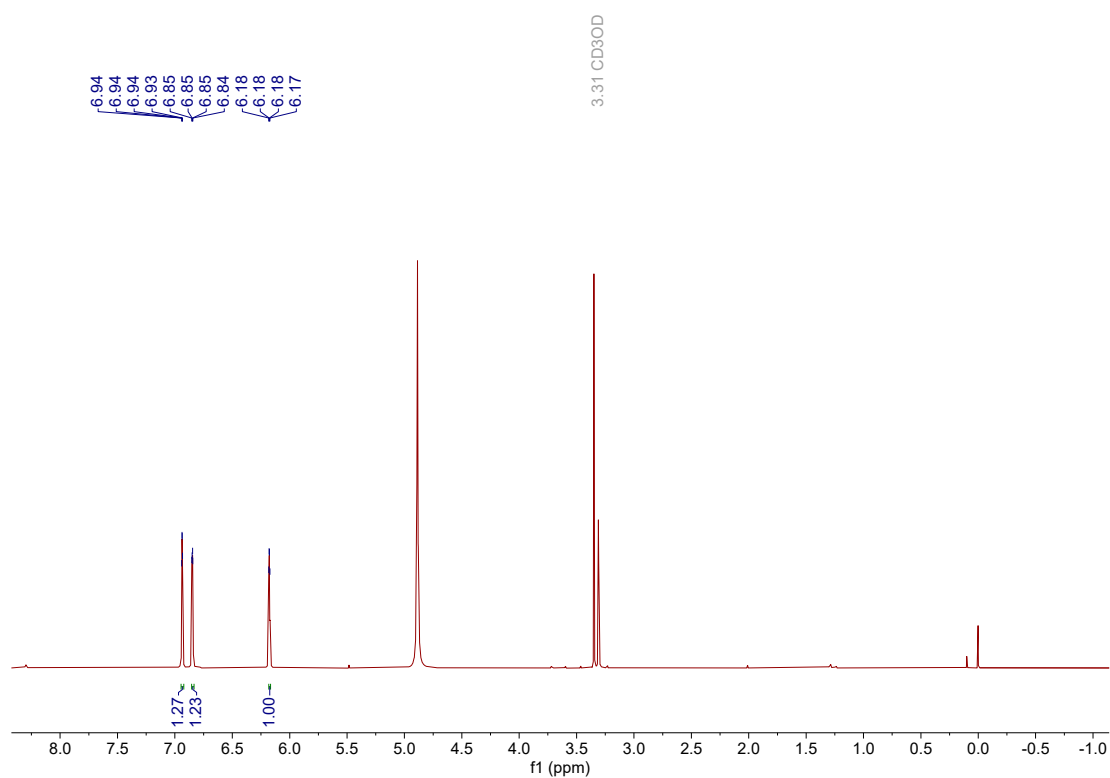
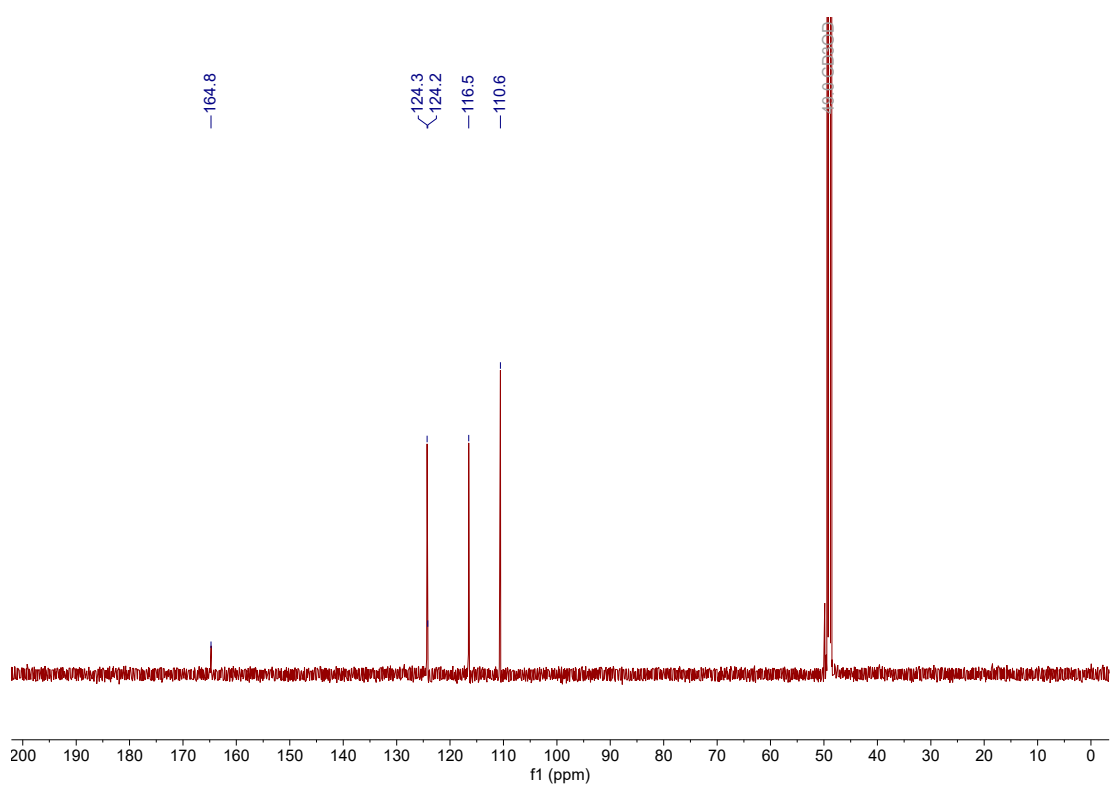
Figure S22a. ¹H NMR spectrum of 22 in DMSO.Figure S22b. ¹³C NMR spectrum of 22 in DMSO.

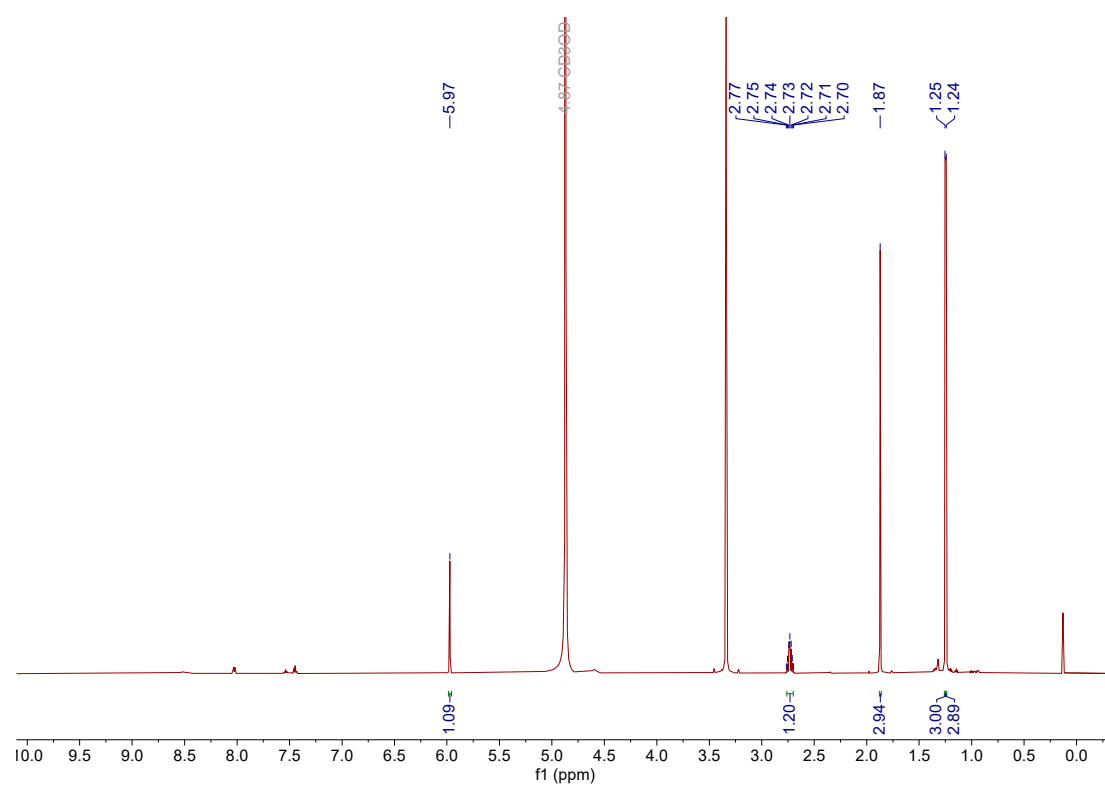
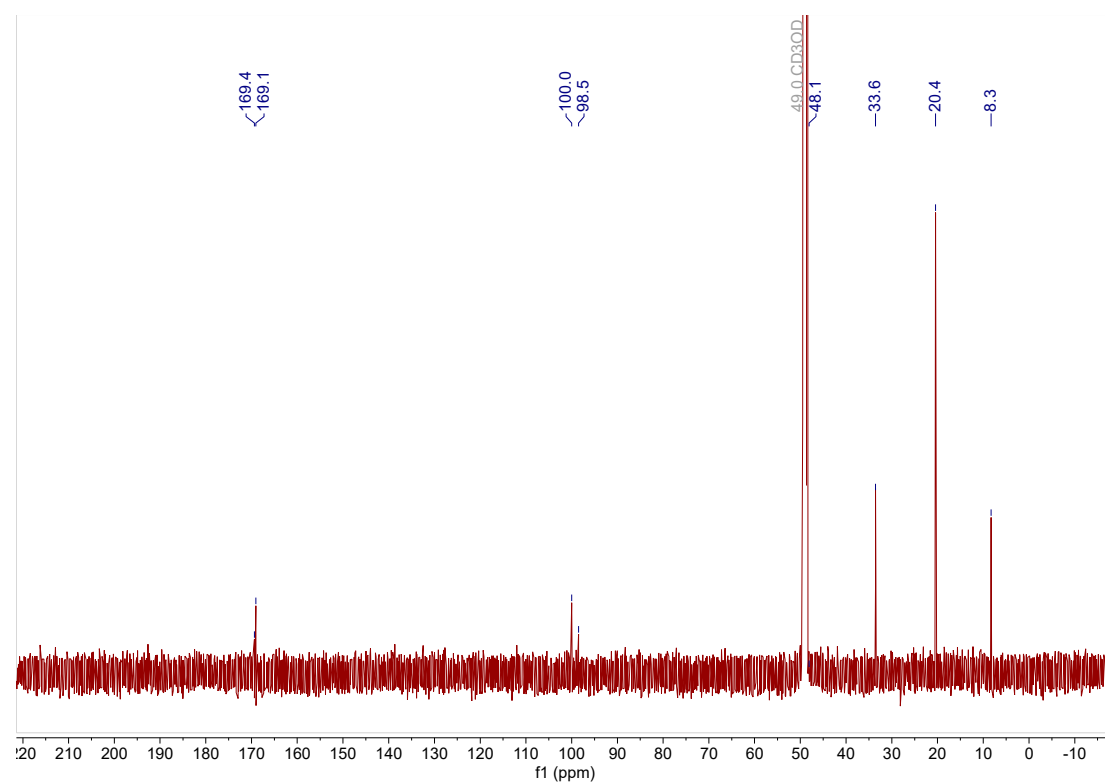
Figure S23a. ¹H NMR spectrum of 23 in DMSO.Figure S23b. ¹³C NMR spectrum of 23 in DMSO.

Figure S24a. ¹H NMR spectrum of **24** in DMSO.Figure S24b. ¹³C NMR spectrum of **24** in DMSO.

Figure S25a. ¹H NMR spectrum of 25 in CD₃OD.Figure S25b. ¹³C NMR spectrum of 25 in CD₃OD.

Figure S26a. ¹H NMR spectrum of 26 in DMSO.Figure S26b. ¹³C NMR spectrum of 26 in DMSO.

Figure S27a. ¹H NMR spectrum of 27 in CD₃OD.Figure S27b. ¹³C NMR spectrum of 27 in CD₃OD.

Figure S28a. ¹H NMR spectrum of 28 in CD₃OD.Figure S28b. ¹³C NMR spectrum of 28 in CD₃OD.

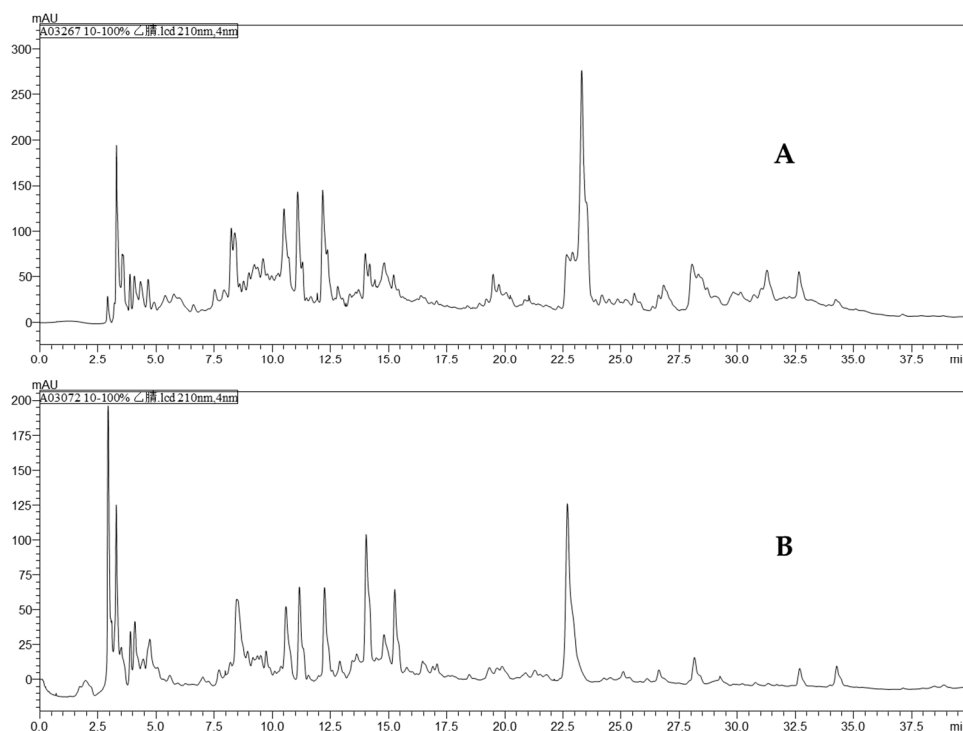


Figure S29. HPLC profiles of residues A and B.

NMR data for 3–28.

Autolytimycin (**3**): white amorphous solid. ^1H NMR (600 MHz, $\text{DMSO}-d_6$): δ 9.32 (s, 1H, HN-22), 6.60 (s, 1H, H-19), 6.25 (s, 1H, H-17), 6.20 (s, 1H, H-21), 5.68 (br s, 1H, H-3), 5.20 (d, $J = 9.6$ Hz, 1H, H-9), 4.84 (d, $J = 7.2$ Hz, 1H, H-7), 4.33 (m, 1H, H-11), 3.30 (s, 3H, $\text{CH}_3\text{O}-6$), 3.21 (s, 3H, $\text{CH}_3\text{O}-12$), 3.19 (m, 1H, H-6), 2.96 (d, $J = 6.0$ Hz, 1H, H-12), 2.29 (m, 1H, H-10), 2.54, 2.28 (m, 2H, H_2-15), 2.16, 2.03 (m, 2H, H_2-4), 1.79 (m, 1H, H-14), 1.70 (s, 3H, H_3-23), 1.36 (s, 3H, H_3-24), 1.23, 1.10 (m, 2H, H_2-5), 1.50, 1.08 (m, 2H, H_2-13), 0.91 (d, $J = 6.6$ Hz, 3H, H_3-25), 0.72 (d, $J = 6.0$ Hz, 3H, H_3-26). ^{13}C NMR (150 MHz, $\text{DMSO}-d_6$): δ 171.1 (C-1), 157.3 ($\text{H}_2\text{N}-\text{CO}_2-7$), 156.1 (C-18), 141.1 (C-16), 140.0 (C-20), 133.9 (C-3), 133.0 (C-9), 131.6 (C-2), 129.8 (C-8), 115.3 (C-21), 112.8 (C-17), 105.8 (C-19), 80.8 (C-7), 80.4 (C-12), 79.2 (C-6), 73.0 (C-11), 58.3 ($\text{CH}_3\text{O}-6$), 56.2 ($\text{CH}_3\text{O}-12$), 42.6 (C-15), 34.0 (C-10), 33.2 (C-13), 30.3 (C-14), 29.5 (C-5), 23.1 (C-4), 18.2 (C-26), 13.3 (C-23), 11.6 (C-24), 11.6 (C-25) [1].

Reblastatin (**4**): white solid. ^1H NMR (600 MHz, CD_3OD): 6.75 (s, 1H, H-19), 6.36 (s, 1H, H-21), 5.89 (br s, 1H, H-3), 5.32 (s, 1H, H-9), 4.97 (d, $J = 7.8$ Hz, 1H, H-7), 3.73 (s, 3H, $\text{CH}_3\text{O}-17$), 3.57 (m, 1H, H-11), 3.47 (s, 3H, $\text{CH}_3\text{O}-6$), 3.37 (s, 3H, $\text{CH}_3\text{O}-12$), 3.34 (m, 1H, H-6), 3.14 (m, 1H, H-12), 2.76, 2.55 (m, 2H, H_2-15), 2.55 (m, 1H, H-10), 2.34, 2.19 (m, 2H, H_2-4), 1.96 (m, 1H, H-14), 1.80 (s, 3H, H_3-23), 1.74, 1.34 (m, 2H, H_2-13), 1.52 (s, 3H, H_3-24), 1.37, 1.15 (m, 2H, H_2-5), 1.04 (d, $J = 6.6$ Hz, 3H, H_3-25), 0.84 (d, $J = 6.6$ Hz, 3H, H_3-26). ^{13}C NMR (150 MHz, CD_3OD): δ 174.9 (C-1), 159.1 ($\text{H}_2\text{N}-\text{CO}_2-7$), 151.7 (C-20), 145.3 (C-17), 136.4 (C-3), 135.7 (C-2), 135.3 (C-16), 134.7 (C-9), 133.0 (C-18), 131.5 (C-8), 118.7 (C-21), 109.6 (C-19), 83.9 (C-7), 82.9 (C-12), 81.2 (C-6), 75.2 (C-11), 60.9 ($\text{CH}_3\text{O}-17$), 59.8 ($\text{CH}_3\text{O}-6$), 57.3 ($\text{CH}_3\text{O}-12$), 37.2 (C-15), 35.8 (C-10), 34.8 (C-13), 32.6 (C-14), 31.3 (C-5), 24.7 (C-4), 19.6 (C-26), 17.4 (C-25), 13.7 (C-23), 12.1 (C-24) [1].

17-*O*-Demethylgeldanamycin (**5**): yellow solid. ^1H NMR (600 MHz, CDCl_3): δ 8.95 (s, 1H, HN-22), 7.41 (s, 1H, H-19), 6.97 (d, $J = 11.4$ Hz, 1H, H-3), 6.57 (t, $J = 11.4$ Hz, 1H, H-4), 5.90 (t, $J = 10.2$ Hz, 1H, H-5), 5.79 (d, $J = 9.6$ Hz, 1H, H-9), 5.18 (s, 1H, H-7), 4.33 (d, $J = 9.0$ Hz, 1H, H-6), 3.55 (m, 1H, H-11), 3.35 (m, 1H, H-12), 3.36 (s, 3H, $\text{CH}_3\text{O}-12$), 3.31 (s, 3H, $\text{CH}_3\text{O}-6$), 2.80 (m, 1H, H-10), 2.44 (m, 2H, H_2-15), 2.03 (s, 3H, H_3-23), 1.80 (s, 3H, H_3-24), 1.77 (m, 2H, H_2-13), 1.74 (m, 1H, H-14), 1.00 (d, $J = 6.6$ Hz, 3H, H_3-25), 0.97 (d, $J = 6.6$ Hz, 3H, H_3-26). ^{13}C NMR (150 MHz, CDCl_3): δ 184.5 (C-21), 183.2 (C-18), 168.3 (C-1), 156.1 ($\text{H}_2\text{N}-\text{CO}_2-7$), 153.2 (C-17), 140.6 (C-20), 137.1

(C-5), 134.8 (C-2), 133.7 (C-8), 133.4 (C-9), 127.7 (C-3), 126.4 (C-4), 117.5 (C-16), 108.3 (C-19), 82.0 (C-7), 81.6 (C-6), 81.1 (C-12), 72.8 (C-11), 57.5 (CH₃O-6), 56.9 (CH₃O-12), 34.6 (C-13), 32.9 (C-15), 32.4 (C-10), 28.2 (C-14), 23.4 (C-26), 13.0 (C-24), 12.6 (C-23), 12.4 (C-25) [2].

Geldanamycin (**6**): yellow solid. ¹H NMR (600 MHz, CDCl₃): δ 8.71 (s, 1H, HN-22), 7.28 (s, 1H, H-19), 6.94 (d, *J* = 11.4 Hz, 1H, H-3), 6.56 (t, *J* = 11.4 Hz, 1H, H-4), 5.87 (t, *J* = 10.2 Hz, 1H, H-5), 5.82 (d, *J* = 10.2 Hz, 1H, H-9), 5.18 (s, 1H, H-7), 4.32 (d, *J* = 8.4 Hz, 1H, H-6), 4.12 (s, 3H, CH₃O-17), 3.54 (d, *J* = 7.0 Hz, 1H, H-11), 3.88–3.39 (m, 1H, H-12), 3.36 (s, 3H, CH₃O-12), 3.29 (s, 3H, CH₃O-6), 2.76–2.79 (m, 1H, H-10), 2.42–2.50 (m, 2H, H₂-15), 2.02 (s, 3H, H₃-23), 1.79 (s, 3H, H₃-24), 1.76–1.77 (m, 2H, H₂-13), 1.64–1.68 (m, 1H, H-14), 0.98 (d, *J* = 6.0 Hz, 3H, H₃-25), 0.97 (d, *J* = 6.0 Hz, 3H, H₃-26). ¹³C NMR (150 MHz, CDCl₃): δ 185.1 (C-21), 184.3 (C-18), 168.3 (C-1), 157.1 (C-17), 156.1 (H₂N-CO₂-7), 138.2 (C-20), 136.6 (C-5), 135.0 (C-2), 133.4 (C-8), 133.3 (C-9), 127.7 (C-16), 127.4 (C-3), 126.5 (C-4), 111.9 (C-19), 81.7 (C-7), 81.4 (C-6), 81.2 (C-12), 72.9 (C-11), 61.8 (CH₃O-17), 57.4 (CH₃O-6), 56.8 (CH₃O-12), 34.8 (C-13), 32.9 (C-15), 32.3 (C-10), 28.1 (C-14), 23.1 (C-26), 13.0 (C-24), 12.7 (C-23), 12.5 (C-25) [2].

Cyclo(D-Trp-L-Tyr) (**7**): white solid. [α]_D²⁰: −120.0 (c 0.1, MeOH). ¹H NMR (600 MHz, CD₃OD): δ 7.60 (d, *J* = 8.0 Hz, 1H, H-4), 7.35 (d, *J* = 8.1 Hz, 1H, H-7), 7.13 (t, *J* = 7.6 Hz, 1H, H-6), 7.06 (t, *J* = 7.5 Hz, 1H, H-5), 7.04 (s, 1H, H-2), 6.63 (d, *J* = 8.5 Hz, 2H, H-18, H-20), 6.47 (d, *J* = 8.5 Hz, 2H, H-17, H-21), 4.18 (m, 1H, H-9), 3.87 (m, 1H, H-12), 3.05 (dd, *J* = 14.6, 4.1 Hz, 1H, H-8a), 2.77 (dd, *J* = 14.6, 5.9 Hz, 1H, H-8b), 2.57 (dd, *J* = 13.7, 3.9 Hz, 1H, H-15a), 1.47 (dd, *J* = 13.7, 8.5 Hz, 1H, H-15b). ¹³C NMR (150 MHz, CD₃OD): δ 170.2 (C-11), 169.5 (C-14), 157.6 (C-19), 138.1 (C-7a), 132.0 (C-17, C-21), 128.9 (C-3a), 127.8 (C-16), 125.9 (C-2), 122.7 (C-6), 120.2 (C-5), 119.9 (C-4), 116.3 (C-18, C-20), 112.5 (C-7), 109.6 (C-3), 57.9 (C-12), 57.1 (C-9), 40.1 (C-15), 31.2 (C-8) [3].

Cyclo(L-Pro-L-Trp) (**8**): white solid. [α]_D²⁰: −55.6 (c 0.09, MeOH). ¹H NMR (600 MHz, CDCl₃): δ 8.20 (s, 1H, H-1), 7.59 (d, *J* = 7.9 Hz, 1H, H-4), 7.40 (d, *J* = 8.2 Hz, 1H, H-7), 7.24 (t, *J* = 7.5 Hz, 1H, H-6), 7.15 (t, *J* = 7.5 Hz, 1H, H-5), 7.11 (s, 1H, H-2), 5.73 (s, 1H, H-10), 4.38 (dd, *J* = 11.0, 3.7 Hz, 1H, H-9), 4.08 (t, *J* = 8.1 Hz, 1H, H-12), 3.77 (dd, *J* = 15.1, 3.8 Hz, 1H, H-8a), 3.66 (m, 1H, H-15a), 3.58 (m, 1H, H-15b), 2.97 (dd, *J* = 15.1, 10.9 Hz, 1H, H-8b), 2.33 (m, 1H, H-13a), 2.01 (m, 2H, H-13b, H-14a), 1.91 (m, 1H, H-14b). ¹³C NMR (150 MHz, CDCl₃): δ 169.5 (C-11), 165.7 (C-17), 136.8 (C-7a), 126.9 (C-3a), 123.4 (C-2), 123.0 (C-6), 120.2 (C-5), 118.7 (C-4), 111.7 (C-7), 110.2 (C-3), 59.4 (C-9), 54.7 (C-12), 45.6 (C-15), 28.5 (C-13), 27.0 (C-8), 22.8 (C-14) [4].

Cyclo(L-Ser-L-Trp) (**9**): yellow oil. [α]_D²⁰: −38.0 (c 0.1, MeOH). ¹H NMR (600 MHz, CD₃OD): δ 7.65 (d, *J* = 7.8 Hz, 1H, H-4), 7.37 (d, *J* = 8.4 Hz, 1H, H-7), 7.14 (t, *J* = 6.6 Hz, 1H, H-6), 7.14 (s, 1H, H-2), 7.04 (t, *J* = 7.8 Hz, 1H, H-5), 4.27 (s, 1H, H-9), 3.85 (d, *J* = 5.4 Hz, 1H, H-12), 3.41 (d, *J* = 11.4 Hz, 2H, H-15), 3.41 (dd, *J* = 11.4, 3.6 Hz, 1H, H-8a), 2.94 (d, *J* = 5.4 Hz, 1H, H-8b). ¹³C NMR (150 MHz, CD₃OD): δ 170.2 (C-14), 168.1 (C-11), 138.0 (C-7a), 128.9 (C-3a), 125.4 (C-2), 122.5 (C-6), 120.1 (C-4), 119.7 (C-5), 112.3 (C-7), 109.9 (C-3), 64.7 (C-15), 58.8 (C-9), 57.5 (C-12), 31.9 (C-8) [5].

Cyclo(L-Tyr-L-Pro) (**10**): white solid. [α]_D²⁰: −72.0 (c 0.1, MeOH). ¹H NMR (600 MHz, CD₃OD): δ 7.07 (d, *J* = 8.5 Hz, 2H, H-2', H-6'), 6.74 (d, *J* = 8.5 Hz, 2H, H-3', H-5'), 4.40 (m, 1H, H-9), 4.08 (m, 1H, H-6), 3.59 (m, 1H, H-3), 3.39 (m, 1H, H-3), 3.10 (m, 2H, H₂-10), 2.13 (m, 1H, H-5), 1.84 (m, 2H, H₂-4), 1.27 (m, 1H, H-5). ¹³C NMR (150 MHz, CD₃OD): δ 170.8 (C-7), 167.0 (C-1), 157.7 (C-4'), 132.1 (C-2', C-6'), 127.7 (C-1'), 116.2 (C-3', C-5'), 60.1 (C-6), 57.9 (C-9), 45.9 (C-3), 37.7 (C-10), 29.4 (C-5), 22.7 (C-4) [6].

Cyclo(L-Ile-L-Tyr) (**11**): white solid. [α]_D²⁰: −24.0 (c 0.1, MeOH). ¹H NMR (600 MHz, CD₃OD): δ 7.02 (d, *J* = 8.5 Hz, 2H, H-13, H-17), 6.69 (d, *J* = 8.5 Hz, 2H, H-14, H-16), 4.26 (m, 1H, H-2), 3.70 (dd, *J* = 4.2, 1.7 Hz, 1H, H-5), 3.18 (m, 1H, H-11a), 2.89 (dd, *J* = 14.0, 4.7 Hz, 1H, H-11b), 1.42 (m, 1H, H-7), 0.80 (m, 1H, H-8), 0.76 (d, *J* = 7.1 Hz, 3H, H₃-10), 0.71 (t, *J* = 7.1 Hz, 3H, H₃-9). ¹³C NMR (150 MHz, CD₃OD): δ 169.9 (C-1, C-4), 157.9 (C-15), 132.6 (C-13, C-17), 127.5 (C-12), 116.3 (C-14, C-16), 60.9 (C-2), 57.4 (C-5), 39.8 (C-7), 38.9 (C-11), 24.7 (C-8), 15.4 (C-10), 11.9 (C-9) [7].

Cyclo(L-Ile-L-Phe) (**12**): white solid. [α]_D²⁰: −8.0 (c 0.1, MeOH). ¹H NMR (600 MHz, DMSO-*d*₆): δ 8.10 (s, 1H, HN-6), 7.88 (s, 1H, HN-3), 7.21 (m, 5H, H-13, H-14, H-15, H-16, H-17), 4.21 (m, 1H, H-5), 3.58 (m, 1H, H-2), 3.15 (m, 1H, H-11a), 2.86 (dd, *J* = 13.5, 5.1 Hz, 1H, H-11b), 1.40 (m, 1H, H-7), 0.65 (m, 2H, H₂-8), 0.57 (m, 3H, H₃-9), 0.56 (d, *J* = 7.1 Hz, 3H, H₃-10). ¹³C NMR (150 MHz, DMSO-*d*₆): δ 166.4 (C-1, C-4), 136.3 (C-12), 130.4 (C-13, C-17), 127.9 (C-14, C-16), 126.5 (C-15), 58.7 (C-2), 55.0 (C-5), 37.8 (C-11), 37.6 (C-7), 23.2 (C-8), 14.4 (C-10), 11.7 (C-9) [8].

Cyclo(4-OH-L-Pro-L-Phe) (**13**): white solid. $[\alpha]_D^{20}$: -84.0 (c 0.1, MeOH), ^1H NMR (600 MHz, CD_3OD): δ 7.20–7.29 (m, 5H, H-2', H-3', H-4', H-5', H-6'), 4.59 (br s, 1H, H-8), 4.51 (td, $J = 4.8, 1.2$ Hz, 1H, H-9), 4.38 (dd, $J = 6.0, 1.2$ Hz, 1H, H-6), 4.28 (t, $J = 4.8$ Hz, 1H, H-4), 3.74 (dd, $J = 12.6, 4.8$ Hz, 1H, H-3b), 3.29 (s, 1H, H-3a), 3.17 (t, $J = 6.0$ Hz, 1H, H-10a), 3.17 (t, $J = 6.0$ Hz, 1H, H-10b), 2.09 (q, $J = 6.0$ Hz, 1H, H-5a), 1.41 (m, 1H, H-5b). ^{13}C NMR (150 MHz, CD_3OD): δ 171.3 (C-7), 167.1 (C-1), 137.4 (C-1'), 131.0 (C-2'), 129.5 (C-3'), 128.0 (C-4'), 68.5 (C-4), 58.3 (C-6), 57.6 (C-9), 55.2 (C-3), 38.9 (C-5), 38.0 (C-10) [9].

Cyclo(L-Ser-L-Phe) (**14**): white solid. $[\alpha]_D^{20}$: -3.3 (c 0.06, MeOH). ^1H NMR (600 MHz, $\text{DMSO}-d_6$): δ 7.99 (d, $J = 2.6$ Hz, 1H, HN-3), 7.89 (d, $J = 2.5$ Hz, 1H, HN-6), 7.28 (t, $J = 7.4$ Hz, 2H, H-3', H-5'), 7.22 (dd, $J = 8.5, 1.6$ Hz, 1H, H-4'), 7.17 (t, $J = 7.3$ Hz, 2H, H-2', H-6'), 4.87 (s, 1H, OH), 4.05 (m, 1H, H-2), 3.66 (m, 1H, H-5), 3.28 (m, 1H, H-7a), 3.10 (dd, $J = 13.5, 6.1$ Hz, 1H, H-8a), 2.98 (dd, $J = 13.5, 5.0$ Hz, 1H, H-8b), 2.85 (dd, $J = 10.8, 5.8$ Hz, 1H, H-7b). ^{13}C NMR (150 MHz, $\text{DMSO}-d_6$): δ 167.5 (C-1), 165.8 (C-4), 136.7 (C-1'), 129.9 (C-6', C-2'), 128.1 (C-5', C-3'), 126.5 (C-4'), 63.1 (C-7), 57.1 (C-5), 55.5 (C-2), 40.1 (C-8) [10].

Cyclo(L-Phe-L-Ala) (**15**): white solid. $[\alpha]_D^{20}$: -10.0 (c 0.1, MeOH), ^1H NMR (600 MHz, CD_3OD): δ 7.20–7.29 (m, 5H, H-2', H-3', H-4', H-5', H-6'), 4.32 (td, $J = 4.8, 1.2$ Hz, 1H, H-2), 3.78 (m, 1H, H-5), 3.28 (dd, $J = 13.8, 4.2$ Hz, 1H, H-8b), 2.98 (dd, $J = 13.8, 4.8$ Hz, 1H, H-8a), 0.54 (d, $J = 6.6$ Hz, 3H, H-3-7). ^{13}C NMR (150 MHz, CD_3OD): δ 170.6 (C-4), 168.5 (C-1), 136.6 (C-1'), 131.8 (C-2'), 129.5 (C-3'), 128.3 (C-4'), 57.4 (C-2), 51.5 (C-5), 40.3 (C-8), 20.4 (C-7) [8].

Cyclo(L-Leu-L-Ile) (**16**): white solid. $[\alpha]_D^{20}$: -16.0 (c 0.1, MeOH), ^1H NMR (600 MHz, CDCl_3): δ 4.02 (m, 1H, H-2), 3.95 (dd, $J = 1.28, 3.68$ Hz, 1H, H-5), 2.13 (m, 1H, H-12), 1.91 (m, 1H, H-7), 1.78 (m, 1H, H-11a), 1.62 (m, 1H, H-11b), 1.47 (m, 1H, H-8a), 1.21 (m, 1H, H-8b), 1.04 (d, $J = 7.2$ Hz, 3H, H-3-10), 1.01 (d, $J = 6.6$ Hz, 3H, H-3-13), 0.95 (d, $J = 6.6$ Hz, 3H, H-3-14), 0.88 (t, $J = 6.6$ Hz, 3H, H-3-9). ^{13}C NMR (150 MHz, CDCl_3): δ 168.5 (C-1), 167.1 (C-4), 60.2 (C-5), 53.2 (C-2), 43.5 (C-11), 38.3 (C-7), 24.5 (C-12), 24.1 (C-8), 23.5 (C-13), 21.1 (C-14), 15.6 (C-10), 11.9 (C-9) [11].

Cyclo(L-Ala-L-Pro) (**17**): white solid. $[\alpha]_D^{20}$: -98.0 (c 0.1, MeOH). ^1H NMR (600 MHz, $\text{DMSO}-d_6$): δ 8.13 (s, 1H, NH), 4.16 (m, 1H, H-2), 4.08 (m, 1H, H-2'), 3.36 (m, 2H, H-5), 2.12 (m, 1H, H-3a), 1.84 (m, 1H, H-3b), 1.84 (m, 2H, H-2-4), 1.21 (d, $J = 6.8$ Hz, 3H, H-3-3'). ^{13}C NMR (150 MHz, $\text{DMSO}-d_6$): δ 169.9 (C-1), 166.5 (C-1'), 58.6 (C-2), 50.1 (C-5), 44.8 (C-2'), 27.6 (C-3), 22.3 (C-4), 15.2 (C-3') [12].

Cyclo(L-Pro-L-Val) (**18**): white solid. $[\alpha]_D^{20}$: -86.0 (c 0.1, MeOH). ^1H NMR (600 MHz, CD_3OD): δ 4.22 (m, 1H, H-2'), 4.05 (t, 1H, $J = 2.1$ Hz, H-2), 3.54 (m, 2H, H-5), 2.50 (m, 1H, H-3'), 2.33 (m, 1H, H-3a), 2.03 (m, 1H, H-3b), 1.96 (m, 2H, H-2-4), 1.10 (d, $J = 7.2$ Hz, 3H, H-3-4'), 0.95 (d, $J = 6.9$ Hz, 3H, H-3-5'). ^{13}C NMR (150 MHz, $\text{DMSO}-d_6$): δ 172.6 (C-1), 167.6 (C-1'), 61.5 (C-2), 60.0 (C-2'), 45.3 (C-5), 29.9 (C-3), 29.5 (C-3'), 23.3 (C-4), 18.8 (C-4'), 16.7 (C-5') [13].

6-(2,3-Dihydroxy-3-methylbutyl)indolin-2-one (**19**): yellow oil. $[\alpha]_D^{20}$: $+6.0$ (c 0.1, MeOH), ^1H NMR (600 MHz, $\text{DMSO}-d_6$): δ 10.31 (s, 1H, H-1), 7.07 (d, $J = 7.8$ Hz, 1H, H-4), 6.78 (d, $J = 9.0$ Hz, 1H, H-5), 6.72 (s, 1H, H-7), 4.41 (d, $J = 6.0$ Hz, 1H, HO-9), 4.24 (s, 1H, HO-10), 3.40 (s, 1H, H-3), 3.27 (dd, $J = 8.4, 4.8$ Hz, 1H, H-9), 2.89 (d, $J = 13.8$ Hz, 1H, H-8a), 2.32 (dd, $J = 13.8, 10.2$ Hz, 1H, H-8b), 1.11 (s, 3H, H-3-11), 1.06 (s, 3H, H-3-12). ^{13}C NMR (150 MHz, $\text{DMSO}-d_6$): δ 176.7 (C-2), 143.5 (C-7a), 140.9 (C-6), 123.8 (C-4), 122.7 (C-3a), 122.1 (C-5), 110.2 (C-7), 79.2 (C-9), 71.7 (C-10), 37.6 (C-8), 35.5 (C-3), 26.9 (C-11), 24.1 (C-12) [14].

17-Hydroxycyclooctatin (**20**): yellow oil. ^1H NMR (600 MHz, CD_3OD): δ 5.39 (m, 1H, H-9), 4.45 (m, 1H, H-5), 3.68 (dd, $J = 10.2, 7.8$ Hz, 1H, H-18), 3.62 (dd, $J = 10.8, 3.6$ Hz, 1H, H-17), 3.56 (dd, $J = 10.8, 6.6$ Hz, 1H, H-18), 3.24 (dd, $J = 10.2, 8.4$ Hz, 1H, H-17), 2.76, 1.94 (m, 2H, H-8), 2.64 (m, 1H, H-3), 2.61 (m, 1H, H-2), 2.39 (m, 1H, H-11), 1.99 (m, 1H, H-6), 1.81 (m, 1H, H-15), 1.72, 1.39 (m, 2H, H-2-4), 1.62, 1.45 (m, 2H, H-2-1), 1.69, 1.23 (m, 2H, H-2-13), 1.67, 1.34 (m, 2H, H-2-12), 1.36 (s, 3H, H-3-19), 1.28 (s, 3H, H-3-20), 1.04 (d, $J = 6.6$ Hz, 3H, H-3-16). ^{13}C NMR (150 MHz, CD_3OD): δ 153.9 (C-10), 119.5 (C-9), 78.3 (C-7), 75.6 (C-5), 65.6 (C-17), 63.4 (C-18), 57.9 (C-6), 52.3 (C-11), 46.6 (C-1), 45.8 (C-14), 45.5 (C-13), 44.9 (C-3), 42.2 (C-8), 39.7 (C-4), 38.7 (C-15), 35.8 (C-2), 26.7 (C-19), 25.9 (C-12), 25.3 (C-20), 17.3 (C-16) [15].

16,17-Dihydroxycyclooctatin (**21**): yellow oil. ^1H NMR (600 MHz, CD_3OD): δ 5.47 (t, $J = 8.4$ Hz, 1H, H-9), 4.49 (t, $J = 4.8$ Hz, 1H, H-5), 3.86 (q, $J = 5.4$ Hz, 1H, H-16), 3.69 (m, 1H, H-16), 3.63 (m, 1H, H-17), 3.61 (m, 2H, H-18), 3.42 (dd, $J = 10.8, 8.4$ Hz, 1H, H-17), 2.80 (t, $J = 11.4$ Hz, 1H, H-8), 2.60–2.66 (m, 3H, H-2, H-3, H-11), 1.95–2.00 (m, 2H, H-6, H-8), 1.93 (m, 1H, H-13), 1.75 (m, 2H, H-4, H-12), 1.67 (m, 1H, H-13), 1.63 (m, 1H, H-1), 1.49 (m, 1H, H-1), 1.42 (m, 1H, H-12), 1.38 (s, 3H, H-3-19), 1.31 (s, 3H, H-3-20), 1.31 (m, 1H, H-4),

1.23 (m, 1H, H-15). ^{13}C NMR (150 MHz, CD_3OD): δ 153.9 (C-10), 118.7 (C-9), 78.3 (C-7), 75.6 (C-5), 63.9 (C-16), 63.4 (C-18), 61.5 (C-17), 58.0 (C-6), 47.2 (C-11), 46.6 (C-1), 45.8 (C-14), 45.7 (C-15), 45.6 (C-13), 44.9 (C-3), 42.2 (C-8), 39.7 (C-4), 35.8 (C-2), 26.7 (C-19), 25.5 (C-20), 25.3 (C-12) [16].

Terragine E (**22**): white solid. ^1H NMR (600 MHz, $\text{DMSO}-d_6$): δ 9.64 (br s, 2H, OH), 7.72 (s, 4H, HN), 3.44 (t, J = 6.6 Hz, 2H, H-18, H-29), 2.97 (dt, J = 7.0, 6.0 Hz, 4H, H-7, H-11, H-22, H-33), 2.57 (t, J = 9.6 Hz, 2H, H-15, H-26), 2.26 (t, J = 6.6 Hz, 2H, H-14, H-25), 2.26 (s, 2H, H-3, H-4), 1.47 (m, 2H, H-19, H-30), 1.34 (m, 4H, H-8, H-10, H-21, H-32), 1.20 (m, 3H, H-9, H-20, H-31). ^{13}C NMR (150 MHz, $\text{DMSO}-d_6$): δ 172.0 (C-16, C-27), 171.5 (C-5, C-13), 171.4 (C-2, C-24), 46.8 (C-18, C-29), 38.3 (C-7, C-11, C-22, C-33), 31.1 (C-3, C-4), 30.0 (C-14, C-25), 28.6 (C-8, C-10, C-21, C-32), 27.5 (C-15, C-26), 25.8 (C-19, C-30), 23.5 (C-9), 23.2 (C-20, C-31) [17].

Deferriferrioxamine E (**23**): white solid. ^1H NMR (600 MHz, $\text{DMSO}-d_6$): δ 9.65 (s, 3H, HO), 7.71 (t, J = 6.0 Hz, 3H, HN), 3.43 (t, J = 7.2 Hz, 6H, H-7, H-18, H-29), 2.96 (dt, J = 7.2, 6.0 Hz, 6H, H-11, H-22, H-33), 2.56 (t, J = 6.0 Hz, 6H, H-4, H-15, H-26), 2.25 (t, J = 7.2 Hz, 6H, H-3, H-14, H-25), 1.46 (m, 6H, H-8, H-19, H-30), 1.34 (m, 6H, H-10, H-21, H-32), 1.19 (m, 6H, H-9, H-20, H-31). ^{13}C NMR (150 MHz, $\text{DMSO}-d_6$): δ 172.1 (C-5, C-16, C-27), 171.6 (C-2, C-13, C-24), 46.9 (C-7, C-18, C-29), 38.4 (C-11, C-22, C-33), 30.1 (C-3, C-14, C-25), 28.6 (C-10, C-21, C-32), 27.5 (C-4, C-15, C-26), 25.9 (C-8, C-19, C-30), 23.2 (C-9, C-20, C-31) [18].

4-(2-Hydroxyethyl)-5-methyloxazole (**24**): white solid. ^1H NMR (600 MHz, $\text{DMSO}-d_6$): δ 8.78 (s, 1H, H-2), 3.56 (t, J = 6.5 Hz, 2H, H-8), 2.87 (t, J = 6.5 Hz, 2H, H-7), 2.30 (s, 3H, H-6). ^{13}C NMR (150 MHz, $\text{DMSO}-d_6$): δ 150.1 (C-2), 148.5 (C-5), 128.4 (C-4), 61.3 (C-8), 29.3 (C-7), 14.7 (C-6) [19].

2,3-Dihydro-2,2-dimethyl-4 (1H)-quinazolinone (**25**): white solid. ^1H NMR (600 MHz, CD_3OD): δ 7.70 (d, J = 7.8 Hz, 1H, H-5), 7.29 (t, J = 8.8 Hz, 1H, H-7), 6.72 (t, J = 8.8 Hz, 1H, H-8), 6.69 (d, J = 8.2 Hz, 1H, H-6), 1.50 (s, 6H, H-9, H-10). ^{13}C NMR (150 MHz, CD_3OD): δ 166.8 (C-4), 148.8 (C-8a), 135.2 (C-7), 128.6 (C-5), 118.5 (C-8), 115.8 (C-6), 114.8 (C-5a), 68.5 (C-2), 29.1 (C-9, C-10) [20].

1H-Pyrrole-2-carboxamide (**26**): white solid. ^1H NMR (600 MHz, $\text{DMSO}-d_6$): δ 11.36 (br s, 1H, H-1), 7.44 (br s, 2H, H-7), 6.83 (m, 1H, H-5), 6.75 (m, 1H, H-3), 6.06 (m, 1H, H-4). ^{13}C NMR (150 MHz, $\text{DMSO}-d_6$): δ 162.3 (C-6), 126.3 (C-2), 121.3 (C-5), 110.6 (C-3), 108.5 (C-4) [21].

1H-Pyrrole-2-carboxylic acid (**27**): white solid. ^1H NMR (600 MHz, CD_3OD): δ 6.94 (dd, J = 2.5, 1.5 Hz, 1H, H-5), 6.85 (dd, J = 3.7, 1.5 Hz, 1H, H-3), 6.18 (dd, J = 3.7, 2.5 Hz, 1H, H-4). ^{13}C NMR (150 MHz, CD_3OD): δ 164.8 (COOH), 124.3 (C-2), 124.2 (C-5), 116.5 (C-3), 110.6 (C-4) [22].

Surugapyrone A (**28**): white solid. ^1H NMR (600 MHz, CD_3OD): δ 5.97 (s, 1H, H-5), 2.72 (m, 1H, H-7), 1.87 (s, 3H, H-10), 1.25 (d, J = 6.6 Hz, 6H, H-8, H-9). ^{13}C NMR (150 MHz, CD_3OD): δ 169.4 (C-6), 169.0 (C-2), 167.9 (C-4), 100.0 (C-3), 98.5 (C-5), 33.5 (C-7), 20.4 (C-8, C-9), 8.8 (C-10) [23].

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