Supporting Information
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Supporting Information

Synthesis of Amino-ADT Provides Access to Hydrolytically-Stable Amide-Coupled Hydrogen Sulfide-Releasing Drug Targets

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Figure S1. HPLC analysis of a) ADT-NH$_2$, ADT-NAc, and the reaction products of ADT-NAc hydrolysis; b) ADT-OH, ADT-OAc, and the reaction products of ADT-OAc hydrolysis. Conditions: 20 µM analyte, 18 hour hydrolysis in 0.1 M HCl, H$_2$O:acetonitrile eluent gradient from 4 to 100 % with 10 mM triethylammonium acetate. Hydrolysis of ADT-OAc does not appear to be entirely clean, as a reaction byproduct was also observed on HPLC.
Figure S2. MTT cell proliferation assay of ADT derivatives (31-900 µM) in HeLa cells. Cells were treated with A) ADT-OH or ADT-NH$_2$ (black), B) ADT-OMe or ADT-NMe$_2$ (red), C) ADT-ORox or ADT-NRox (green), D) ADT-OVal or ADT-NVal (blue) for 24 hours.
**Materials and methods.** Reagents were purchased from Sigma-Aldrich or Tokyo Chemical Industry (TCI) and used as received. ADT-OH, ADT-OMe, and ADT-OVal were synthesized as reported previously with modifications as described below.1-2 Deuterated solvents were purchased from Cambridge Isotope Laboratories and used as received. Silica gel (SiliaFlash F60, Silicycle, 230 - 400 mesh) was used for column chromatography. Preparatory chromatography was performed on Silicycle SiliaPlates (1 mm thickness). 1H and 13C{1H} NMR spectra were recorded on a Varian INOVA 500 MHz NMR instrument. Chemical shifts are reported in ppm relative to residual protic solvent resonances. UV–visible spectra were acquired on a Cary 100 spectrometer equipped with a Quantum Northwest TLC-42 dual cuvette temperature controller at 37.00 ± 0.05 °C. HPLC samples were analyzed using reverse-phase HPLC (Akta purifier; Amersham Biosciences) on a C18 column (Hypersil GOLD, 5 mm 4.6/250 mm; Thermo Scientific).

**Spectroscopic materials and methods.** Stock solutions of ADT-OH, ADT-OMe, ADT-OVal, ADT-ORox, ADT-NVal, and ADT-NRox were prepared in an N2-filled glovebox and stored at -25 °C until immediately before use. Spectroscopic measurements were obtained using septum-sealed cuvettes obtained from Starna Scientific.

**5-(4-Methoxyphenyl)-3H-1,2-dithiole-3-thione (ADT-OMe):** Anethole (4.15 g, 28.0 mmol) and sulfur (6.00 g, 187 mmol) were dissolved in DMF (25 mL) and refluxed at 170 °C under N2 for 8 hours. After the reaction flask was cooled to room temperature, the reaction mixture was diluted into water and extracted into toluene. The toluene fractions were dried with Na2SO4 and concentrated, and the remaining solid was recrystallized from 5% methanol/DCM. These crystals were then further purified by column chromatography (4:1 Hex:EtOAc) to give pure product as a brownish-red crystalline solid (2.27 g, 34% yield). 1H NMR (500 MHz, DMSO) δ (ppm): 7.87
(d, J = 8.8 Hz, 2H), 7.75 (s, 1H), 7.07 (d, J = 8.8 Hz, 2H), 3.84 (s, 3H). $^{13}$C{$^1$H} NMR (125 MHz, DMSO) δ (ppm): 214.70, 173.77, 162.66, 134.11, 128.98, 123.64, 115.02, 55.63.

5-(4-Hydroxyphenyl)-3H-1,2-dithiole-3-thione (ADT-OH): ADT-OMe (2.00 g, 8.32 mmol), and anhydrous pyridine hydrochloride (5.77 g, 49.9 mmol) were added to an oven-dried pressure vessel under N₂. The apparatus was submerged into an oil bath and stirred at 220 °C. After stirring for 25 minutes, the reaction flask was cooled to room temperature, and the contents were dissolved in methanol and transferred to a round bottom flask. The methanol was removed, and the contents of the round bottom were dissolved in a 50:50 mixture of 0.5 M HCl and EtOAc in order to solubilize the crude product. This mixture was then further diluted with water and extracted into EtOAc. The organic layer was dried with Na₂SO₄ and purified by column chromatography (3:2 Hex:EtOAc) to afford ADT-OH as a lovely golden orange solid (1.60 g, 85%). $^1$H NMR (500 MHz, DMSO) δ (ppm): 10.49 (s, 1H), 7.78 (d, J = 7.8 Hz, 2H), 7.69 (s, 1H), 6.89 (d, J = 7.8 Hz, 2H). $^{13}$C{$^1$H} NMR (125 MHz, DMSO) δ (ppm): 214.38, 174.39, 161.75, 133.45, 129.19, 122.13, 116.42.

(E)-tert-Butyl (4-(prop-1-en-1-yl)phenyl)carbamate (1): In a glovebox, 4-chloro-(N-Boc)aniline (350 mg, 1.54 mmol), potassium trans-1-propenyltrifluoroborate (273 mg, 1.85 mmol), Pd(OAc)$_2$ (35 mg, 0.16 mmol), RuPhos (144 mg, 0.308 mmol), and Cs₂CO₃ (1.5 g, 4.6 mmol) were added to an oven-dried 3-neck round bottom flask fitted with a reflux condenser. The sealed apparatus was removed from the glovebox, and a degassed solvent mixture of 4:1 THF:water (10 mL) was added via syringe; minimal solvent aids with full conversion and overall yield. The reaction mixture was stirred at 80 °C under N₂ for 14 hrs, after which the solvent was removed by rotary evaporation. The residue was dissolved in EtOAc and filtered through celite. The filtrate was washed with water, brine, and dried with Na₂SO₄. The crude product was
purified using column chromatography (20-50% Hex:EtOAc gradient) and further purified by recrystallization from hexanes to afford the pure product as a light brown solid (318 mg, 88% yield). \( ^1H \) NMR (500 MHz, DMSO) \( \delta \) (ppm): 9.31 (s, 1H), 7.38 (d, \( J = 8.5 \) Hz, 2H), 7.24 (d, \( J = 8.6 \) Hz, 2H), 6.31 (dd, \( J = 15.8, 1.43 \) Hz, 1H), 6.11-6.18 (m, 1H), 1.81 (dd, \( J = 6.56, 1.5 \) Hz, 3H), 1.47 (s, 9H). \( ^{13}C\{^1H\} \) NMR (125 MHz, DMSO) \( \delta \) (ppm): 152.67, 138.26, 131.34, 130.41, 125.94, 123.34, 118.08, 78.95, 28.11, 18.19. HRMS \([M + Na]^+\) calcd for \([NaC_{14}H_{19}NO_2]^+\) 256.1313; found, 256.1309.

5-(4-Aminophenyl)-3H-1,2-dithiole-3-thione (ADT-NH2): Compound 1 (100 mg, 0.429 mmol) and sulfur (96 mg, 3.0 mmol) were added to an oven-dried pressure vessel and dissolved in DMA (6 mL) under \( N_2 \), and the reaction was stirred at 180 °C for 18 hours. After stirring, the solvent was removed under vacuum whilst heated at 40 °C. The crude residue was diluted with water, extracted into EtOAc. The combined organic fractions were washed with brine and dried with \( Na_2SO_4 \). The compound was purified using column chromatography (3% MeOH:DCM) to afford the pure product as a dark brown solid (66 mg, 68% yield). \( ^1H \) NMR (500 MHz, CD\(_2\)Cl\(_2\)) \( \delta \) (ppm): 7.51 (d, \( J = 8.7 \) Hz, 2H), 7.36 (s, 1H), 6.71 (d, \( J = 8.7 \) Hz, 2H), 4.27 (br, 2H). \( ^{13}C\{^1H\} \) NMR (125 MHz, CD\(_2\)Cl\(_2\)) \( \delta \) (ppm): 215.05, 174.86, 151.60, 133.66, 129.25, 121.63, 115.29. HRMS \([M + H]^+\) calcd for \([C_{9}H_{8}NS_{3}]^+\) 225.9819; found, 225.9823.

(E)-N,N-Dimethyl-4-(prop-1-en-1-yl)aniline (N,N-Dimethyl propenylaniline): In a glovebox, 4-bromo-N,N-dimethylaniline (250 mg, 1.25 mmol), potassium \( trans \)-1-propenyltrifluoroborate (222 mg, 1.50 mmol), Pd(OAc)\(_2\) (14 mg, 0.062 mmol), RuPhos (58 mg, 0.12 mmol), and Cs\(_2\)CO\(_3\) (1.22 g, 3.75 mmol) were added to an oven-dried 3-neck round bottom flask fitted with a reflux condenser. The sealed apparatus was removed from the box, and a degassed solvent mixture of 4:1 THF:water (10 mL) was added via syringe. The mixture was stirred at 80 °C under \( N_2 \) for 12
hrs, after which the solvent was removed by rotary evaporation. The residue was dissolved in EtOAc and filtered through celite. The filtrate was washed with water, brine, and dried with Na₂SO₄. The compound was purified using column chromatography (20-50% Hex:EtOAc gradient) to afford the pure product as a brown solid (163 mg, 81% yield). ¹H NMR (500 MHz, CD₂Cl₂) δ (ppm): 7.20 (d, J = 8.7 Hz, 2H), 6.66 (d, J = 8.8 Hz, 2H), 6.31 (d, J = 17.1 Hz, 1H), 5.96-6.08 (m 1H), 2.92 (s, 6H), 1.84 (d, J = 8.8 Hz, 3H). ¹³C{¹H} NMR (125 MHz, CD₂Cl₂) δ (ppm): 150.17, 131.07, 126.93, 121.53, 112.86, 40.76, 30.15, 18.57.

**5-(4-(Dimethylamino)phenyl)-3H-1,2-dithiole-3-thione (ADT-NMe₂):** N,N-dimethyl propenylaniline (163 mg, 1.01 mmol) and sulfur (227 mg, 7.08 mmol) were added to an oven-dried pressure vessel and dissolved in DMA (6 mL) under N₂, and the reaction was stirred at 180 °C for 18 hours. After stirring, the solvent was removed under vacuum whilst heated at 40 °C. The crude residue was dissolved in EtOAc and washed with water, brine, and dried with Na₂SO₄. The compound was purified using column chromatography (1% MeOH:DCM) to afford the pure product as a brown solid (150 mg, 59% yield). ¹H NMR (500 MHz, CD₂Cl₂) δ (ppm): 7.58 (d, J = 8.8 Hz, 2H), 7.37 (s, 1H), 6.7 (d, J = 8.8 Hz, 2H), 3.06 (s, 6H). ¹³C{¹H} NMR (125 MHz, CD₂Cl₂) δ (ppm): 214.23, 175.22, 153.72, 132.72, 128.98, 119.11, 112.30, 40.44. HRMS [M]⁺ calcd for [C₁₁H₁₁NS₃]⁺ 253.0053; found, 253.0046.

**4-(3-Thioxo-3H-1,2-dithiol-5-yl)phenyl acetate (ADT-OAc):** ADT-OH (50 mg, 0.22 mmol), acetyl chloride (17 mg, 0.22 mmol), and triethylamine (67 mg, 0.66 mmol) were dissolved in dry THF (2 mL) and stirred at room temperature under N₂. After 22 hours the solvent was removed by rotary evaporation, and the residue was purified by preparative chromatography (3:2 Hex:EtOAc) (16 mg, 22% yield). ¹H NMR (500 MHz, CD₂Cl₂) δ (ppm): 7.72 (d, J = 8.6 Hz, 2H), 7.42 (s, 1H), 7.25 (d, J = 8.6 Hz, 2H), 2.31 (s, 3H). ¹³C{¹H} NMR (125 MHz, CD₂Cl₂) δ
(ppm): 216.21, 172.56, 169.38, 154.28, 136.61, 129.75, 128.79, 123.50, 21.48. HRMS [M]^+ calcd for [C_{11}H_{8}O_{3}S]^{+} 267.9686; found, 267.9694.

N-(4-(3-Thioxo-3H-1,2-dithiol-5-yl)phenyl)acetamide (ADT-NAc): ADT-NH_2 (50 mg, 0.22 mmol), acetyl chloride (17 mg, 0.22 mmol), and triethylamine (67 mg, 0.66 mmol) were dissolved in dry THF (2 mL) and stirred at room temperature under N_2. After 22 hours the solvent was removed by rotary evaporation, and the residue was purified by preparative chromatography (3:1 Hex:EtOAc) (11 mg, 19% yield). ^1H NMR (500 MHz, (CD_3)_2CO) δ (ppm): 9.53 (br, 1H), 7.85 (m, 4H), 7.56 (s, 1H), 2.13 (s, 3H). ^13C{^1H} NMR (125 MHz, (CD_3)_2CO) δ (ppm): 216.54, 174.12, 169.47, 144.35, 135.41, 128.80, 126.97, 120.22, 24.43. HRMS [M]^+ calcd for [C_{11}H_{8}NOS]^{+} 266.9846; found, 266.9843.

(S)-4-(3-Thioxo-3H-1,2-dithiol-5-yl)phenyl 2-(6-methoxynaphthalen-2-yl)propanoate (ADT-ORox): Naproxen (50 mg, 0.22 mmol), ADT-OH (49 mg, 0.22 mmol), EDC·HCl (42 mg, 0.22 mmol), and 4-dimethylaminopyridine (3 mg, 0.03 mmol) were dissolved in dry THF (4 mL) and stirred at room temperature under N_2 for 24 hours. After stirring, the solvent was removed under vacuum. The crude residue was dissolved in EtOAc and washed with water, brine, and dried with Na_2SO_4. The crude product was purified via preparative TLC (3:2 Hex:EtOAc) to afford the pure product as a dark red solid (14 mg, 15% yield). ^1H NMR (500 MHz, CD_2Cl_2) δ (ppm): 7.75-7.79 (m, 3H), 7.77 (m, 2H), 7.50 (dd, J= 8.4, 1.9 Hz, 1H), 7.39 (s, 1H), 7.14-7.17 (m, 4H), 4.11-4.16 (q, J = 7.2 Hz, 1H), 3.92 (s, 1H), 1.69 (d, J = 7.2 Hz, 3H). ^13C{^1H} NMR (125 MHz, CD_2Cl_2) δ (ppm): 216.18, 173.21, 172.52, 158.48, 154.44, 136.60, 135.38, 134.50, 129.77, 129.52, 128.75, 127.95, 126.70, 126.61, 123.30, 119.70, 110.57, 106.13, 55.87, 46.12, 18.75. HRMS [M + H]^+ calcd for [C_{23}H_{19}O_{3}S]^{+} 439.0496; found, 439.0476.
4-(3-thioxo-3H-1,2-dithiol-5-yl)phenyl 2-propylpentanoate (ADT-OVal): Valproic acid (32 mg, 0.22 mmol), ADT-OH (52 mg, 0.22 mmol), EDC·HCl (44 mg, 0.22 mmol), and 4-dimethylaminopyridine (2 mg, 0.02 mmol) were dissolved in dry THF (4 mL) and stirred at room temperature under N₂ for 24 hours. After stirring, the solvent was removed under vacuum. The crude residue was dissolved in EtOAc and washed with water, brine, and dried with Na₂SO₄. The crude product was purified via preparative TLC (3:2 Hex:EtOAc) to afford the pure product as a dark red solid (52 mg, 67% yield). ¹H NMR (500 MHz, CD₂Cl₂) δ (ppm): 7.72 (d, J = 8.8 Hz, 2H), 7.43 (s, 1H), 7.22 (d, J = 8.8 Hz, 2H), 2.61-2.67 (m, 1H), 1.71-1.78 (m, 2H), 1.55-1.62 (m, 2H), 1.40-1.48 (m, 4H), 0.97 (t, J = 7.3 Hz, 6H). ¹³C{¹H} NMR (125 MHz, CD₂Cl₂) δ (ppm): 216.03, 174.80, 172.46, 154.32, 136.42, 129.49, 128.61, 123.38, 45.74, 34.91, 21.09, 14.19.

(S)-2-(6-methoxynaphthalen-2-yl)-N-(4-(3-thioxo-3H-1,2-dithiol-5-yl)phenyl)propanamide (ADT-NRox): In a glovebox, naproxen (24 mg, 0.10 mmol), ADT-NH₂ (26 mg, 0.12 mmol), EDC·HCl (20 mg, 0.10 mmol), and 4-dimethylaminopyridine (2 mg, 0.02 mmol) were added to an oven-dried pressure vessel and dissolved in dry CHCl₃ (4 mL) under N₂, and the reaction was stirred at 120 °C for 27 hours. After stirring, the reaction mixture was diluted with DCM and washed with 0.1 M HCl, 0.5 M K₂CO₃, and brine. The organic layer was dried with Na₂SO₄, and purified by preparative TLC (1:1 Hex:EtOAc) to afford the pure product as a dark red solid (9 mg, 18% yield). ¹H NMR (500 MHz, CD₂Cl₂) δ (ppm): 7.74-7.78 (m, 3H), 7.59 (m, 4H), 7.44 (dd, J = 8.5, 1.8 Hz, 1H), 7.38 (br, 1H), 7.37 (s, 1H), 7.15-7.18 (m, 2H), 3.91 (s, 3H), 3.88 (q, J = 7.1 Hz, 1H), 1.64 (d, J = 7.1 Hz, 3H). ¹³C{¹H} NMR (125 MHz, CD₂Cl₂) δ (ppm): 215.84, 173.18, 173.10, 158.54, 142.42, 136.22, 135.62, 134.56, 129.73, 129.58, 128.37, 128.32, 127.43, 126.90, 126.55, 120.31, 119.83, 106.19, 55.88, 48.73, 18.93. HRMS [M + H]⁺ calcd for [C₂₃H₁₉NO₂S₃]⁺ 438.0656; found, 438.0645.
2-Propyl-N-(4-(3-thioxo-3H-1,2-dithiol-5-yl)phenyl)pentanamide (ADT-NVal): In a glovebox, ADT-NH$_2$ (200 mg, 0.888 mmol), 2-propylpentanoic acid (192 µL, 1.20 mmol), EDC·HCl (230 mg, 1.20 mmol), and 4-dimethylaminopyridine (15 mg, 0.12 mmol) were added to an oven-dried pressure vessel and dissolved in dry CHCl$_3$ (8 mL) under N$_2$, and the reaction stirred at 120 °C for 2.5 days. The reaction mixture was diluted with DCM and washed with 0.1 M HCl, 0.5 M K$_2$CO$_3$, and brine. The organic layer was dried with Na$_2$SO$_4$ and purified via column chromatography (20-50% Hex:EtOAc gradient). Pure product was obtained as an orange-red solid (170 mg, 54% yield). $^1$H NMR (500 MHz, CD$_2$Cl$_2$) $\delta$ (ppm): 7.71 (d, J = 8.8 Hz, 2H), 7.66 (d, J= 8.8 Hz, 2H), 7.42 (s, 1H), 7.39 (br, 1H), 2.24 (m, 1H), 1.63-1.70 (m, 2H), 1.45-1.52 (m, 2H), 1.32-1.39 (m, 4H), 0.92 (t, J = 7.3 Hz, 6H). $^{13}$C{$^1$H} NMR (125 MHz, CD$_2$Cl$_2$) $\delta$ (ppm): 215.90, 175.26, 173.28, 142.48, 135.65, 128.42, 127.41, 120.44, 49.37, 35.76, 21.37, 14.48. HRMS [M]$^+$ calcd for [C$_{17}$H$_{21}$NOS$_3$]$^+$ 351.0785; found, 351.0773.

Hydrolysis of ADT-OAc and ADT-NAc. A cuvette was charged with 3.00 mL of 0.10 M HCl. After addition of an ADT-OAc or ADT-NAc stock solution (60 µL, 1.0 M in DMSO) via syringe, a UV-vis spectrum was recorded at 0, 60, 120, 240, 540, and 1080 minutes. Each reaction cuvette was incubated at 37 °C during the course of the experiment. Percent hydrolysis values were calculated relative to ADT-OH or ADT-NH$_2$ absorbances (20 µM in 0.10 M HCl) at 358 or 311 nm, respectively.

MTT Assay$^3$ of ADT Derivatives. C6 cells were seeded at 2,500 cells per well on a 96 well plate the night before drug treatment to allow for adherence of the cells to the bottom of the wells. The following day, cells were treated with ADT derivatives (31, 55, 95, 170, 290, 510, and 900 µM) for 24 hours at 37 °C and 5% CO$_2$. MTT (3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyl tetrazolium bromide) was dissolved in PBS at 5 mg/mL and filtered to sterilize and remove any
insoluble residue present. The MTT solution (10 µL) was added to all wells and was incubated at 37 °C for 3.5 hours. The solution was removed and 100 µL of acidic isopropanol (0.04 M HCl, 0.01% IGEPAL in isopropanol) was added to all wells and placed on a shaker for 15 minutes in the dark at room temperature. After incubation, the plate was read on a Tecan Safire2 UV-vis plate reader at 570 nm.

References

NMR Spectra

5-(4-methoxyphenyl)-3H-1,2-dithiole-3-thione (ADT-OMe)

$^1$H NMR (500 MHz, DMSO)

$^{13}$C{$^1$H} NMR (125 MHz, DMSO)
5-(4-hydroxyphenyl)-3H-1,2-dithiole-3-thione (ADT-OH)

$^1$H NMR (300 MHz, DMSO)

$^{13}$C($^1$H) NMR (125 MHz, DMSO)
(E)-tert-butyl (4-(prop-1-en-1-yl)phenyl)carbamate (1)

$\text{H NMR (500 MHz, DMSO)}$

$\text{C}^{13}\text{H NMR (125 MHz, DMSO)}$

$\text{H}_2\text{O}$

$\text{H}_2\text{O}$
5-(4-aminophenyl)-3H-1,2-dithiole-3-thione (ADT-NH$_2$)

$^1$H NMR (500 MHz, CD$_2$Cl$_2$)

$^{13}$C{$^1$H} NMR (125 MHz, CD$_2$Cl$_2$)
(E)-N,N-dimethyl-4-(prop-1-en-1-yl)aniline (N,N-Dimethyl Propenylaniline)

$^1$H NMR (500 MHz, CD$_2$Cl$_2$)

$^1^3$C{$^1$H} NMR (125 MHz, CD$_2$Cl$_2$)
5-(4-(dimethylamino)phenyl)-3H-1,2-dithiole-3-thione (ADT-NMe₂)

¹H NMR (500 MHz, CD₂Cl₂)

¹³C{¹H} NMR (125 MHz, CD₂Cl₂)
4-(3-thioxo-3H-1,2-dithiol-5-yl)phenyl acetate (ADT-OAc)

$\text{H NMR (500 MHz, CD}_2\text{Cl}_2$)

$\text{C\{H\} NMR (125 MHz, CD}_2\text{Cl}_2$)

$\text{H}_2\text{O}$

$\text{H NMR (500 MHz, CD}_2\text{Cl}_2$)

$\text{C\{H\} NMR (125 MHz, CD}_2\text{Cl}_2$)
N-(4-(3-thioxo-3H-1,2-dithiol-5-yl)phenyl)acetamide (ADT-NAc)

$^1$H NMR (500 MHz, (CD$_3$)$_2$CO)

$^{13}$C{$^1$H} NMR (125 MHz, (CD$_3$)$_2$CO)
(S)-4-(3-thioxo-3H-1,2-dithiol-5-yl)phenyl 2-(6-methoxynaphthalen-2-yl)propanoate (ADT-ORox)

$^1$H NMR (500 MHz, CD$_2$Cl$_2$)

$^{13}$C($^1$H) NMR (125 MHz, CD$_2$Cl$_2$)
4-(3-thioxo-3H-1,2-dithiol-5-yl)phenyl 2-propylpentanoate (ADT-OVal)

$^{1}$H NMR (500 MHz, CD$_2$Cl$_2$)

$^{13}$C($^1$H) NMR (125 MHz, CD$_2$Cl$_2$)
(S)-2-(6-methoxynaphthalen-2-yl)-N-(4-(3-thioxo-3H-1,2-dithiol-5-yl)phenyl)propanamide (ADT-NRox)

$^1$H NMR (500 MHz, CD$_2$Cl$_2$)

$^{13}$C($^1$H) NMR (125 MHz, CD$_2$Cl$_2$)
2-propyl-N-(4-(3-thioxo-3H-1,2-dithio-5-yl)phenyl)pentanamide (ADT-NVal)

$^1$H NMR (500 MHz, CD$_2$Cl$_2$)

$^{13}$C{$^1$H} NMR (125 MHz, CD$_2$Cl$_2$)