Supplementary Information

Three-component reaction for a rapid access to underexplored 1,3-thiazine-2-thiones

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Experimental procedures

General Methods

Synthetic procedures, conducted under argon atmosphere, were performed on a vacuum line using standard Schlenk techniques. Preparative column chromatography was carried out using GRACE SiO_2 (0.035–0.070 mm, type KG 60). TLC was performed on MACHERY-NAGEL SiO_2 F254 plates on aluminum sheets. Melting points were obtained on a melting point apparatus of LABORATORY DEVICES and are uncorrected. ^1H and ^{13}C NMR spectra were recorded with a BRUKER AMX R 500 (measuring frequency: ^1H NMR = 500.1 MHz, ^{13}C NMR = 125.8 MHz) or a BRUKER Avance III 500 (measuring frequency: ^1H NMR = 499.9 MHz, ^{13}C NMR = 125.7 MHz) spectrometer in $CDCl_3$ solution. Chemical shifts are referenced to the residual peaks of the solvent [$CDCl_3$: 7.26 ppm (^1H NMR), 77.16 ppm (^{13}C NMR)][S1]. Assignments of the signals were supported by measurements applying DEPT, COSY and HMBC techniques. Mass spectra were obtained on a WATERS Q-TOF Premier. The IR spectra were recorded with a BRUKER Tensor 27 spectrometer equipped with a "Golden Gate" diamond-ATR (attenuated total reflection) unit. (*EZ*)-3-Chloro-2,3-diphenylacrylaldehyde[S2] (**1a**), (*EZ*)-3-chloro-3-(4-hydroxyphenyl)-2-phenylacrylaldehyde[S3] (**1b**), (*EZ*)-3-chloro-3-(4-chlorophenyl)-2-phenylacrylaldehyde[S4] (**1c**), (*E*)-3-chloro-2,3-bis(4-methoxyphenyl)acrylaldehyde[S5] (**1d**), (*EZ*)-3-chloro-2,3-bis(4-nitrophenyl)acrylaldehyde[3] (**1e**), 2-chloro-1-cyclohexene-1-carboxaldehyde[S5] (**1f**), and 3-chloro-3-methyl-2-phenylacrylaldehyde[S6] (**1g**) were prepared according to published procedures. DCM was refluxed with CaH_2 and freshly distilled prior to use. Toluene was refluxed with Na and freshly distilled prior to use. Et_3N was dried over molecular sieves (3 Å) and freshly distilled prior to use. MeCN was dried over molecular sieves (3 Å) and freshly distilled prior to use.

General Procedure (GP A)

The respective β-chlorovinyl aldehyde (1.0 equiv.) was dissolved in anhydrous MeCN (2 mL per mmol β-chlorovinyl aldehyde). The respective amine (1.5 equiv.) in anhydrous MeCN (3 mL per mmol β-chlorovinyl aldehyde), CS_2 (3.0 equiv.) and anhydrous Et_3N (0.5 equiv.) were added at 0 °C. After stirring overnight at 0 °C the solvent was removed via high-vacuum low-temperature distillation. In a final step the crude product was purified by column chromatography on silica gel.

(*RS*)-3-Allyl-4-hydroxy-5,6-diphenyl-3,4-dihydro-2*H*-1,3-thiazine-2-thione (2a): Following **GP A**, aldehyde (*EZ*)-**1a** (243 mg, 1.00 mmol), allylamine (86 mg, 1.50 mmol), CS_2 (228 mg, 3.00 mmol) and anhydrous Et_3N (51 mg, 0.50 mmol) were used. Column chromatography (DCM; R_f = 0.23) afforded the desired thiazinethione **2a** (304 mg, 90%) as a yellow solid, mp 110–112 °C (from DCM/*n*-hexane); IR (ATR): $\tilde{\nu}$ 3272, 2054, 3019, 2923, 1643, 1156, 1127, 760, 731 cm^{-1}; ^1H NMR (500.1 MHz, $CDCl_3$): δ 3.89–3.91 (1 H, m, OH), 4.68–4.72 (1 H, m, NCH_2), 5.18–5.22 (1 H, m, NCH_2), 5.26–5.28 (1 H, m, CH=CH_2), 5.30–5.33 (1 H, m, CH=CH_2), 5.75 (1 H, d, ^3J = 9.2 Hz, NCH), 5.94–6.02 (1 H, m, CH=CH_2), 7.20–7.28 (10 H, m, 10 CH_{Ar}) ppm; ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 55.41 (NCH_2), 84.72 (NCH), 119.51 (CH=CH_2), 127.41 (CHC=C), 127.91 (*p*-CH_{Ar}), 128.54, 128.65, 128.89 (6 CH_{Ar}), 129.22 (*p*-CH_{Ar}), 130.05 (2 CH_{Ar}), 131.49 (NCH_2CH), 134.08 (C_{Ar}CS), 135.79 (C_{Ar}CCH), 137.09 (CHC=C), 189.48 (C=S) ppm; MS (ESI): m/z 362.1 (M+Na^+, 10%), 322.0 (M–OH^+, 100%), 279.0 (M–COS^+, 10%); HRMS (ESI): Found 362.0660; Calc. for $C_{19}H_{17}NNaOS_2$ $[M+Na]^+$ 362.0649.

(*RS*)-4-Hydroxy-3-(2-methylallyl)-5,6-diphenyl-3,4-dihydro-2*H*-1,3-thiazine-2-thione (2b): Following **GP A**, aldehyde (*EZ*)-**1a** (485 mg, 2.00 mmol), 2-methylallylamine (213 mg, 3.00 mmol), CS_2 (457 mg, 6.00 mmol) and anhydrous Et_3N (102 mg, 1.00 mmol) were used. Column chromatography (*n*-hexane/DCM 1:4; R_f = 0.30) afforded the desired thiazinethione **2b** (559 mg, 79%) as a colorless solid, mp 114–116 °C (from DCM/*n*-hexane); IR (ATR): $\tilde{\nu}$ 3268, 2979, 2922, 1492, 1447, 1403, 1339, 1234, 1150, 1099, 1033, 1013, 976, 921, 893, 730 cm^{-1}; ^1H NMR (500.1 MHz, $CDCl_3$): δ 1.73 (3 H, s, CH_3), 3.61 (1 H, d, ^3J = 10.0 Hz, OH), 4.42 (1 H, d, ^2J = 15.4 Hz, NCH_2), 4.86–4.88 (1 H, m, C=CH_2), 4.90–

4.92 (1 H, m, C=CH_2), 5.41 (1 H, d, ^2J = 15.4 Hz, NCH_2), 5.68 (1 H, d, ^3J = 10.0 Hz, NCH), 7.15–7.26 (10 H, m, 10 CH_{Ar}) ppm; ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 20.32 (CH_3), 57.75 (NCH_2), 84.30 (NCH), 114.35 (C=*C*H_2), 127.69 (CH*C*=C), 128.00, 128.65, 128.72, 128.81, 129.33, 130.13 (10 CH_{Ar}), 134.05 (*C*$_{Ar}$CS), 135.79 (*C*$_{Ar}$CCH), 137.14 (CHC=*C*), 139.58 (*C*=CH_2), 189.58 (C=S) ppm; MS (ESI): m/z 376.1 ($M+Na^+$, 10%), 336.1 ($M–OH^+$, 100%); HRMS (ESI): Found 376.0808; Calc. for $C_{20}H_{19}NNaOS_2$ $[M+Na]^+$ 376.0806.

(*RS*)-3-(But-3-en-1-yl)-4-hydroxy-5,6-diphenyl-3,4-dihydro-2*H*-1,3-thiazine-2-thione (2c): Following **GP A**, aldehyde (*EZ*)-**1a** (243 mg, 1.00 mmol), but-3-en-1-amine (107 mg, 1.50 mmol), CS_2 (228 mg, 3.00 mmol) and anhydrous Et_3N (51 mg, 0.50 mmol) were used. Column chromatography (DCM; R_f = 0.22) afforded the desired thiazinethione **2c** (228 mg, 64%) as a yellow solid, mp 133 °C (from DCM/*n*-hexane); IR (ATR): $\tilde{\nu}$ 3262, 3060, 3015, 2986, 2937, 1641, 1169, 1130, 758, 728 cm^{-1}; ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 2.55–2.67 (2 H, m, NCH_2CH_2), 3.59–3.72 (1 H, m, OH), 4.15–4.22 (1 H, m, NCH_2), 4.37–4.44 (1 H, m, NCH_2), 5.01–5.03 (1 H, m, CH=CH_2), 5.09–5.13 (1 H, m, CH=CH_2), 5.70 (1 H, d, ^3J = 9.8 Hz, NCH), 5.74–5.85 (1 H, m, C*H*=CH_2), 7.18–7.27 (10 H, m, CH_{Ar}) ppm; ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 32.25 (NCH_2CH_2), 53.85 (NCH_2), 86.46 (NCH), 118.20 (CH=*C*H_2), 127.49 (CH*C*=C), 127.99 (*p*-CH_{Ar}), 128.61, 128.72, 128.88 (6 CH_{Ar}), 129.33 (*p*-CH_{Ar}), 130.16 (2 CH_{Ar}), 134.05 (*C*$_{Ar}$CS), 134.50 (CH_2=*C*H), 135.78 (*C*$_{Ar}$CCH), 137.20 (CHC=*C*), 188.66 (C=S) ppm; MS (ESI): m/z 376.0 ($M+Na^+$, 100%), 336.1 ($M–OH^+$, 45%), 292.1 ($M–COS^+$, 20%); HRMS (ESI): Found 376.0803; Calc. for $C_{20}H_{19}NNaOS_2$ $[M+Na]^+$ 376.0806.

(*RS*)-3-(But-3-in-1-yl)-4-hydroxy-5,6-diphenyl-3,4-dihydro-2*H*-1,3-thiazine-2-thione (2d): Following **GP A**, aldehyde (*EZ*)-**1a** (486 mg, 2.00 mmol), but-3-in-1-amine (207 mg, 3.00 mmol), CS_2 (456 mg, 6.00 mmol) and anhydrous Et_3N (102 mg, 1.00 mmol) were used. Column chromatography (DCM; R_f = 0.33) afforded the desired thiazinethione **2d** (232 mg, 33%) as a yellow oil; IR (ATR): $\tilde{\nu}$ 3293, 3254, 3054, 3028, 2933, 1486, 1148, 757, 722, 695 cm^{-1}; ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 1.83 (1 H, t, ^4J = 2.6 Hz, C≡CH), 2.74–2.87 (2 H, m, NCH_2CH_2), 4.27–4.34 (1 H, m, NCH_2), 4.42–4.46 (1 H, m, NCH_2), 5.97 (1 H, s, NCH), 7.19–7.31 (10 H, m, 10 CH_{Ar}) ppm; ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 17.68 (NCH_2CH_2), 52.73 (NCH_2), 71.02 (C≡*C*H), 81.47 (*C*≡CH), 86.99 (NCH), 127.40 (CH*C*=C), 127.74 (*p*-CH_{Ar}), 128.36, 128.56, 128.88 (6 CH_{Ar}), 129.13 (*p*-CH_{Ar}), 130.10 (2 CH_{Ar}), 134.04 (*C*$_{Ar}$CS), 135.51 (*C*$_{Ar}$CCH), 137.34 (CHC=*C*), 189.43 (C=S) ppm; MS (ESI): m/z 374.0 ($M+Na^+$, 55%), 334.1 ($M–OH^+$, 100%), 290.1 ($M–COS^+$, 85%); HRMS (ESI): Found 374.0646; Calc. for $C_{20}H_{17}NNaOS_2$ $[M+Na]^+$ 374.0649.

(*RS*)-4-Hydroxy-3-(pent-4-in-1-yl)-5,6-diphenyl-3,4-dihydro-2*H*-1,3-thiazine-2-thione (2e): Following **GP A**, aldehyde (*EZ*)-**1a** (243 mg, 1.00 mmol), pent-4-in-1-amine (125 mg, 1.50 mmol), CS_2 (228 mg, 3.00 mmol) and anhydrous Et_3N (51 mg, 0.50 mmol) were used. Column chromatography (*n*-hexane/DCM/EtOAc 10:2:1; R_f = 0.14) afforded the desired thiazinethione **2e** (194 mg, 53%) as a yellow oil; IR (ATR): $\tilde{\nu}$ 3360, 3292, 3055, 3025, 2931, 1486, 1143, 757, 726, 695 cm^{-1}; ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 1.98 (1 H, t, ^4J = 2.6 Hz, C≡CH), 2.07–2.18 (2 H, m, NCH_2CH_2), 2.25–2.38 (2 H, m, $NCH_2CH_2CH_2$), 4.09 (1 H, d, ^3J = 10.2 Hz, OH), 4.24–4.30 (1 H, m, NCH_2), 4.47–4.53 (1 H, m, NCH_2), 5.85 (1 H, d, ^3J = 10.2 Hz, NCH), 7.25–7.33 (10 H, m, 10 CH_{Ar}) ppm; ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 16.00 ($NCH_2CH_2CH_2$), 26.32 (NCH_2CH_2), 53.52 (NCH_2), 69.72 (C≡*C*H), 82.87 (*C*≡CH), 86.56 (NCH), 127.51 (CH*C*=C), 127.97 (*p*-CH_{Ar}), 128.57, 128.68, 128.87 (6 CH_{Ar}), 129.28 (*p*-CH_{Ar}), 130.09 (2 CH_{Ar}), 133.98 (*C*$_{Ar}$CS), 135.63 (*C*$_{Ar}$CCH), 137.04 (CHC=*C*), 188.82 (C=S) ppm; MS (ESI): m/z 388.0 ($M+Na^+$, 70%), 348.0 ($M–OH^+$, 100%), 304.1 ($M–COS^+$, 50%); HRMS (ESI): Found 388.0813; Calc. for $C_{21}H_{19}NNaOS_2$ $[M+Na]^+$ 388.0806.

(*RS*)-3-Butyl-4-hydroxy-5,6-diphenyl-3,4-dihydro-2*H*-1,3-thiazine-2-thione (2f): Following **GP A**, aldehyde (*EZ*)-**1a** (243 mg, 1.00 mmol), *n*-butylamine (110 mg, 1.50 mmol), CS_2 (228 mg, 3.00 mmol) and anhydrous Et_3N (51 mg, 0.50 mmol) were used. Column chromatography (DCM; R_f = 0.22) afforded

the desired thiazinethione **2f** (171 mg, 48%) as a yellow solid, mp 43–44 °C (from DCM/*n*-hexane); IR (ATR): $\tilde{\nu}$ 3297, 3058, 3017, 2952, 2930, 1599, 1489, 1464, 1444, 1425, 1377, 1232, 757, 727, 694 cm^{-1}; ^1H NMR (500.1 MHz, $CDCl_3$): δ 0.97 (3 H, t, ^3J = 7.3 Hz, CH_3), 1.38–1.43 (2 H, m, CH_2CH_3), 1.82–1.86 (2 H, m, NCH_2CH_2), 3.89–3.97 (1 H, m, OH), 4.09–4.15 (1 H, m, NCH_2), 4.41–4.46 (1 H, m, NCH_2), 5.77 (1 H, d, ^3J = 10.4 Hz, NCH), 7.25–7.33 (10 H, m, CH_{Ar}) ppm; ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 13.85 (CH_3), 20.11 (CH_2CH_3), 29.91 (NCH_2CH_2), 54.26 (NCH_2), 86.08 (NCH), 127.45 (CHC=C), 127.97 (*p*-CH_{Ar}), 128.60, 128.68, 128.87 (6 CH_{Ar}), 129.27 (*p*-CH_{Ar}), 130.13 (2 CH_{Ar}), 134.04 (C_{Ar}CS), 135.80 (C_{Ar}CCH), 137.17 (CHC=*C*), 188.27 (C=S) ppm; MS (ESI): m/z 356.1 ($M+H^+$, 30%), 338.0 ($M–OH^+$, 100%), 294.1 ($M–COS^+$, 9%); HRMS (ESI): Found 356.1132; Calc. for $C_{20}H_{22}NNaOS_2$ $[M+Na]^+$ 356.1143.

(*RS*)-3-Cyclohexyl-4-hydroxy-5,6-diphenyl-3,4-dihydro-2*H*-1,3-thiazine-2-thione (2g): Following **GP A**, aldehyde (*EZ*)-**1a** (243 mg, 1.00 mmol), cyclohexylamine (149 mg, 1.50 mmol), CS_2 (228 mg, 3.00 mmol) and anhydrous Et_3N (51 mg, 0.50 mmol) were used. Column chromatography (DCM; R_f = 0.21) afforded the desired thiazinethione **2g** (269 mg, 70%) as a yellow oil; IR (ATR): $\tilde{\nu}$ 3321, 3083, 3057, 2927, 2855, 1599, 1488, 1468, 1458, 1444, 1244, 1136, 756, 717, 775, 697 cm^{-1}; ^1H NMR (500.1 MHz, $CDCl_3$): δ 1.08–1.19 (2 H, m, 2 $CH_{2,Cy}$), 1.35–1.72 (4 H, m, 4 $CH_{2,Cy}$), 1.77–1.80 (1 H, m, $CH_{2,Cy}$), 1.86–1.88 (2 H, m, 2 $CH_{2,Cy}$), 2.32–2.35 (1 H, m, $CH_{2,Cy}$), 5.44–5.52 (1 H, m, NCH_{Cy}), 5.77 (1 H, s, C*H*OH), 7.13–7.24 (10 H, m, 10 CH_{Ar}) ppm; ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 25.42 ($CH_{2,Cy}$), 25.90 ($CH_{2,Cy}$), 25.99 ($CH_{2,Cy}$), 31.00 ($CH_{2,Cy}$), 31.64 ($CH_{2,Cy}$), 61.37 (NCH_{Cy}), 84.30 (CHOH), 124.50 (CH*C*=C), 127.68 (*p*-CH_{Ar}), 128.54, 128.56 (4 CH_{Ar}), 129.00 (*p*-CH_{Ar}), 129.12, 129.85 (4 CH_{Ar}), 134.38 (C_{Ar}CS), 137.70 (C_{Ar}CCH), 137.88 (CHC=*C*), 191.03 (C=S) ppm; MS (ESI): m/z 404.1 ($M+Na^+$, 70%), 363.1 ($M–OH^+$, 35%), 320.1 ($M–COS^+$, 40%); HRMS (ESI): Found 404.1108; Calc. for $C_{22}H_{23}NNaOS_2$ $[M+Na]^+$ 404.1119.

(*RS*)-3-Benzyl-4-hydroxy-5,6-diphenyl-3,4-dihydro-2*H*-1,3-thiazine-2-thione (2h): Following **GP A**, aldehyde (*EZ*)-**1a** (243 mg, 1.00 mmol), benzylamine (161 mg, 1.50 mmol), CS_2 (228 mg, 3.00 mmol) and anhydrous Et_3N (51 mg, 0.50 mmol) were used. Column chromatography (DCM; R_f = 0.21) afforded the desired thiazinethione **2h** (352 mg, 90%) as a yellow solid, mp 221–222 °C (from DCM/*n*-hexane); IR (ATR): $\tilde{\nu}$ 3307, 3058, 3020, 2929, 1598, 1481, 1443, 1229, 757, 728, 694 cm^{-1}; ^1H NMR (500.1 MHz, $CDCl_3$): δ 3.14 (1 H, d, ^3J = 9.0 Hz, OH), 5.24 (1 H, d, ^3J = 15.0 Hz, NCH_2), 5.63 (1 H, d, ^3J = 9.0 Hz, NCH), 5.64 (1 H, d, ^3J = 15.0 Hz, NCH_2), 6.92–6.94 (2 H, m, 2 CH_{Ar}), 7.01–7.05 (3 H, m, 3 CH_{Ar}), 7.11–7.16 (5 H, m, 5 CH_{Ar}), 7.19–7.23 (3 H, m, 3 CH_{Ar}), 7.28–7.30 (2 H, m, 2 CH_{Ar}) ppm; ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 55.90 (NCH_2), 84.88 (NCH), 127.54 (CH*C*=C), 127.92 (*p*-CH_{Ar}), 128.22 (2 CH_{Ar}), 128.40 (*p*-CH_{Ar}), 128.55, 128.71, 128.79, 129.14 (8 CH_{Ar}), 129.30 (*p*-CH_{Ar}), 130.05 (2 CH_{Ar}), 134.06 (C_{Ar}CS), 135.56 ($C_{Ar}CH_2$), 135.87 (C_{Ar}CCH), 137.01 (CHC=*C*), 190.05 (C=S) ppm; MS (ESI): m/z 390.0 ($M+H^+$, 40%), 372.0 ($M–OH^+$, 100%), 328.0 ($M–COS^+$, 10%); HRMS (ESI): Found 390.0975; Calc. for $C_{23}H_{20}NOS_2$ $[M+H]^+$ 390.0986.

(*RS*)-4-Hydroxy-3-(4-methoxybenzyl)-5,6-diphenyl-3,4-dihydro-2*H*-1,3-thiazine-2-thione (2i): Following **GP A**, aldehyde (*EZ*)-**1a** (243 mg, 1.00 mmol), 4-methoxybenzylamine (206 mg, 1.50 mmol), CS_2 (228 mg, 3.00 mmol) and anhydrous Et_3N (51 mg, 0.50 mmol) were used. Column chromatography (DCM; R_f = 0.11) afforded the desired thiazinethione **2i** (224 mg, 53%) as a yellow oil; IR (ATR): $\tilde{\nu}$ 3301, 3055, 3025, 2955, 2935, 1585, 1481, 1442, 1245, 757, 730, 695 cm^{-1}; ^1H NMR (500.1 MHz, $CDCl_3$): δ 3.77 (3 H, s, OCH_3), 5.33 (1 H, d, ^3J = 14.6 Hz, NCH_2), 5.62 (1 H, d, ^3J = 14.6 Hz, NCH_2), 5.76 (1 H, s, NCH), 6.83–6.84 (2 H, m, 2 CH_{Ar}), 7.03–7.05 (2 H, m, 2 CH_{Ar}), 7.12–7.14 (3 H, m, 3 CH_{Ar}), 7.22–7.27 (5 H, m, 5 CH_{Ar}), 7.34–7.35 (2 H, m, 2 CH_{Ar}) ppm; ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 55.34 (OCH_3), 55.40 (NCH_2), 84.56 (NCH), 114.49 [2 *m*-$CH_{Ar}(CH_2)$], 127.42 (CH*C*=C), 127.62 ($C_{Ar}CH_2$), 127.84 (*p*-CH_{Ar}), 128.50, 128.65, 128.82 (6 CH_{Ar}), 129.21 (*p*-CH_{Ar}), 129.79 [2 *o*-$CH_{Ar}(CH_2)$], 130.05 (2 CH_{Ar}), 134.13 (C_{Ar}CS), 135.82 (C_{Ar}CCH), 137.10 (CHC=*C*), 159.63 [*p*-$C_{Ar}(CH_2)$], 189.82 (C=S) ppm; MS (ESI): m/z

442.0 (M+Na$^+$, 100%), 402.1 (M–OH$^+$, 75%); HRMS (ESI): Found 442.0914; Calc. for $C_{24}H_{21}NNaO_2S_2$ [M+Na]$^+$ 442.0911.

(*RS*)-3-(2-Bromophenethyl)-4-hydroxy-5,6-diphenyl-3,4-dihydro-2*H*-1,3-thiazine-2-thione (2j): Following **GP A**, aldehyde (*EZ*)-**1a** (243 mg, 1.00 mmol), 2-bromophenethylamine (300 mg, 1.50 mmol), CS_2 (228 mg, 3.00 mmol) and anhydrous Et_3N (51 mg, 0.50 mmol) were used. Column chromatography (DCM; R_f = 0.26) afforded the desired thiazinethione **2j** (429 mg, 89%) as a colorless solid, mp 164–166 °C (from DCM/*n*-hexane); IR (ATR): $\tilde{\nu}$ 3347, 3060, 3052, 2962, 2925, 2854, 1495, 1472, 1443, 1405, 1335, 1253, 1146, 1102, 1071, 1045, 1005, 981, 927, 888, 779, 714, 659 cm^{-1}; ^{1}H NMR (499.9 MHz, $CDCl_3$): δ 3.19–3.25 (1 H, m, $C_{Ar}CH_2$), 3.34–3.40 (1 H, m, $C_{Ar}CH_2$), 3.74 (1 H, d, ^3J = 10.3 Hz, OH), 4.16–4.22 (1 H, m, NCH_2), 4.77–4.83 (1 H, m, NCH_2), 5.45 (1 H, d, ^3J = 10.3 Hz, NCH), 6.89–6.90 [1 H, m, *p*-C*H*$_{Ar}$(CH$_2$)], 7.01–7.03 (2 H, m, 2 CH_{Ar}), 7.11–7.16 (4 H, m, 4 CH_{Ar}), 7.21–7.26 (6 H, m, 6 CH_{Ar}), 7.35 (1 H, dd, ^3J = 8.0 Hz, ^4J = 0.8 Hz, *o*-CH_{Ar}Br) ppm; ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 33.93 ($C_{Ar}CH_2$), 54.17 (NCH_2), 86.93 (NCH), 124.43 (C_{Ar}Br), 127.35 (CH*C*=C), 127.78, 127.81, 128.35, 128.53, 128.71, 128.88, 129.23, 130.03, 131.28 (13 CH_{Ar}), 132.94 (*o*-CH_{Ar}Br), 134.21 (C_{Ar}CS), 135.36 (CHC=*C*), 136.79 (C_{Ar}CCH), 137.47 ($C_{Ar}CH_2$), 188.88 (C=S) ppm; MS (ESI): m/z 504.0 (M+Na$^+$, 90%), 464.0 (M–OH$^+$, 50%), 434.7 (M–COS$^+$, 10%); HRMS (ESI): Found 504.0065; Calc. for $C_{24}H_{20}BrNNaOS_2$ [M+Na]$^+$ 504.0067.

(*RS*)-3-Allyl-4-hydroxy-6-(4-hydroxyphenyl)-5-phenyl-3,4-dihydro-2H-1,3-thiazine-2-thione (2k): Following GP A, aldehyde (*EZ*)-**1b** (259 mg, 1.00 mmol), allylamine (86 mg, 1.50 mmol), CS_2 (228 mg, 3.00 mmol) and anhydrous Et_3N (51 mg, 0.50 mmol) were used. Column chromatography (DCM/EtOAc 9:1; R_f = 0.31) afforded the desired thiazinethione **2k** (152 mg, 43%) as a red oil; IR (ATR): $\tilde{\nu}$ 3331, 3214, 2982, 1641, 1159, 1124, 765, 730 cm^{-1}; ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 1.64 (1 H, bs, C_{Ar}OH), 3.19 (1 H, s, CHO*H*), 4.66–4.70 (1 H, m, NCH_2), 5.03–5.08 (1 H, m, NCH_2), 5.21–5.24 (1 H, m, CH=CH_2), 5.23–5.27 (1 H, m, CH=CH_2), 5.65 (1 H, s, NCH), 5.89–5.97 (1 H, m, C*H*=CH_2), 6.62–6.64 [2 H, m, 2 *o*-CH_{Ar}(OH)], 7.05–7.07 [2 H, m, 2 *m*-CH_{Ar}(OH)], 7.14–7.16 (5 H, m, 5 CH_{Ar}) ppm; ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 55.62 (NCH_2), 85.04 (NCH), 115.80 [2 *o*-CH_{Ar}(OH)], 119.59 (CH=*C*H$_2$), 126.20 (C_{Ar}CS), 126.68 (CH*C*=C), 127.88 (*p*-CH_{Ar}), 128.66, 128.84 (4 CH_{Ar}), 131.59 (*C*H=CH_2), 131.68 [2 *m*-CH_{Ar}(OH)], 135.62 (C_{Ar}CCH), 137.34 (CHC=*C*), 156.67 (CH_{Ar}OH), 189.51 (C=S) ppm; MS (ESI): m/z 378.0 (M+Na$^+$, 50%), 338.0 (M–OH$^+$, 100%), 294.0 (M–COS$^+$, 12%); HRMS (ESI): Found 378.0588; Calc. for $C_{19}H_{17}NNaO_2S_2$ [M+Na]$^+$ 378.0598.

(*RS*)-3-Allyl-6-(4-chlorophenyl)-4-hydroxy-5-phenyl-3,4-dihydro-2*H*-1,3-thiazine-2-thione (2l): Following **GP A**, aldehyde (*EZ*)-**1c** (554 mg, 2.00 mmol), allylamine (171 mg, 3.00 mmol), CS_2 (457 mg, 6.00 mmol) and anhydrous Et_3N (102 mg, 1.00 mmol) were used. Column chromatography (*n*-hexane/DCM 3:7; R_f = 0.11) afforded the desired thiazinethione **2l** (284 mg, 38%) as a yellow oil; IR (ATR): $\tilde{\nu}$ 3317, 3082, 2923, 1482, 1442, 1413, 1398, 1333, 1288, 1236, 1157, 1125, 1089, 1013, 984, 925, 904, 821, 765, 730, 698 cm^{-1}; ^{1}H NMR (499.9 MHz, $CDCl_3$): δ 3.66 (1 H, d, ^3J = 9.3 Hz, OH), 4.70–4.74 (1 H, m, NCH_2), 5.06–5.10 (1 H, m, NCH_2), 5.25–5.28 (1 H, m, CH=CH_2), 5.28–5.32 (1 H, m, CH=CH_2), 5.71 (1 H, d, ^3J = 9.3 Hz, NCH), 5.93–6.01 (1 H, m, C*H*=CH_2), 7.15–7.22 (9 H, m, 9 CH_{Ar}) ppm; ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 55.57 (NCH_2), 84.78 (NCH), 119.77 (CH=*C*H$_2$), 127.90 (CH*C*=C), 128.23, 128.79, 128.83, 129.05, 131.41 (9 CH_{Ar}), 131.50 (*C*H=CH_2), 132.54 (C_{Ar}Cl), 134.67 (C_{Ar}CS), 135.38 (CHC=*C*), 136.79 (C_{Ar}CCH), 189.05 (C=S) ppm; MS (ESI): m/z 396.0 (M+Na$^+$, 100%), 356.0 (M–OH$^+$, 100%); HRMS (ESI): Found 396.0255; Calc. for $C_{19}H_{16}ClNNaOS_2$ [M+Na]$^+$ 396.0260.

(*RS*)-3-Allyl-4-hydroxy-5,6-bis(4-methoxyphenyl)-3,4-dihydro-2*H*-1,3-thiazine-2-thione (2m): Following **GP A**, aldehyde (*E*)-**1d** (908 mg, 3.00 mmol), allylamine (257 mg, 4.50 mmol), CS_2 (685 mg, 9.00 mmol) and anhydrous Et_3N (153 mg, 1.50 mmol) were used. Column chromatography (DCM; R_f = 0.14) afforded the desired thiazinethione **2m** (935 mg, 78%) as a colorless oil; IR (ATR): $\tilde{\nu}$ 3351, 2932, 2836, 1603, 1506, 1483, 1440, 1414, 1334, 1293, 1244, 1174, 1157, 1114, 1089, 1028, 989, 925, 905,

826, 795, 734, 656 cm^{-1}; ^1H NMR (499.9 MHz, $CDCl_3$): δ 3.75 (3 H, s, OCH_3), 3.76 (3 H, s, OCH_3), 4.66–4.71 (1 H, m, NCH_2), 5.13–5.17 (1 H, m, NCH_2), 5.23–5.25 (1 H, m, CH=CH_2), 5.26–5.30 (1 H, m, CH=CH_2), 5.67 (1 H, s, NCH), 5.91–5.99 (1 H, m, CH=CH_2), 6.71–6.75 [4 H, m, 4 *o*-CH_{Ar}(OCH_3)], 7.09–7.11 [2 H, m, 2 *o*-CH_{Ar}(CCH)], 7.17–7.19 [2 H, m, 2 *o*-CH_{Ar}(CS)] ppm; ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 55.33 [*p*-($C_{Ar}OCH_3$)(CCH)], 55.38 [*p*-($C_{Ar}OCH_3$)(CS)], 55.50 (NCH_2), 85.14 (NCH), 114.07 [2 *m*-CH_{Ar}(CS)], 114.20 [2 *m*-CH_{Ar}(CCH)], 119.40 (CH=CH_2), 126.31 (C_{Ar}CS), 126.46 (CHC=C), 129.71 (C_{Ar}CCH), 130.13 [2 *o*-CH_{Ar}(CCH)], 131.49 [2 *o*-CH_{Ar}(CS)], 131.64 (CH=CH_2), 134.22 (CHC=C), 159.16 [*p*-C_{Ar}(CCH)], 160.23 [*p*-C_{Ar}(CS)], 189.45 (C=S) ppm; MS (ESI): m/z 422.1 ($M+Na^+$, 100%), 382.1 ($M–OH^+$, 40%); HRMS (ESI): Found 422.0848; Calc. for $C_{21}H_{21}NNaO_3S_2$ $[M+Na]^+$ 422.0861.

(*RS*)-3-Allyl-4-hydroxy-5,6-bis(4-nitrophenyl)-3,4-dihydro-2*H*-1,3-thiazine-2-thione (2n): Following **GP A**, aldehyde (*E*)-**1d** (998 mg, 3.00 mmol), allylamine (257 mg, 4.50 mmol), CS_2 (685 mg, 9.00 mmol) and anhydrous Et_3N (153 mg, 1.50 mmol) were used. Column chromatography (DCM/EtOAc 19:1; R_f = 0.48) afforded the desired thiazinethione **2n** (516 mg, 40%) as a red solid, mp 194–195 °C (from DCM/*n*-hexane); IR (ATR): $\tilde{\nu}$ 2930, 2835, 1659, 1602, 1508, 1295, 1244, 1174, 1145, 1025, 828, 730 cm^{-1}; ^1H NMR (500.1 MHz, $CDCl_3$): δ 4.65–4.70 (1 H, m, NCH_2), 5.12–5.16 (1 H, m, NCH_2), 5.27–5.35 (2 H, m, CH=CH_2), 5.72 (1 H, s, NCH), 5.92–6.00 (1 H, m, CH=CH_2), 7.33–7.35 [2 H, m, 2 *o*-CH_{Ar}(CCH)], 7.42–7.45 [2 H, m, 2 *o*-CH_{Ar}(CS)], 8.05–8.07 [2 H, m, 2 *m*-CH_{Ar}(CCH)], 8.09–8.12 [2 H, m, 2 *m*-CH_{Ar}(CS)] ppm; ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 55.42 (NCH_2), 83.68 (NCH), 120.33 (CH=CH_2), 124.17, 124.26 [4 *o*-CH_{Ar}(NO_2)], 126.91 (CHC=C), 129.80 [2 *o*-CH_{Ar}(CCH)], 131.13 [2 *o*-CH_{Ar}(CS)], 131.20 (CH=CH_2), 137.05 (C_{Ar}CCH), 139.95 (C_{Ar}CS), 142.90 (CHC=C), 147.37 [*p*-C_{Ar}(CCH)], 148.32 [*p*-C_{Ar}(CS)], 187.82 (C=S) ppm;

(*RS*)-4-Hydroxy-5,6-bis(4-methoxyphenyl)-3-(2-methylallyl)-3,4-dihydro-2*H*-1,3-thiazine-2-thione (2o): Following **GP A**, aldehyde (*E*)-**1d** (606 mg, 2.00 mmol), 2-methylallylamine (213 mg, 3.00 mmol), CS_2 (457 mg, 6.00 mmol) and anhydrous Et_3N (102 mg, 1.00 mmol) were used. Column chromatography (DCM; R_f = 0.22) afforded the desired thiazinethione **2o** (550 mg, 67%) as a yellow solid, mp 67–69 °C (from DCM/*n*-hexane); IR (ATR): $\tilde{\nu}$ 3306, 2933, 2835, 1603, 1506, 1483, 1335, 1292, 1247, 1175, 1142, 1114, 1090, 1029, 979, 950, 909, 827, 795, 779, 660 cm^{-1}; ^1H NMR (500.1 MHz, $CDCl_3$): δ 1.72 (3 H, s, CH_3), 3.49 (1 H, d, ^3J = 10.2 Hz, OH), 3.76 (3 H, s, OCH_3), 3.77 (3 H, s, OCH_3), 4.40 (1 H, d, ^2J = 15.4 Hz, NCH_2), 4.85–4.87 (1 H, m, C=CH_2), 4.90–4.91 (1 H, m, C=CH_2), 5.41 (1 H, d, ^2J = 15.4 Hz, NCH_2), 5.63 (1 H, d, ^3J = 10.2 Hz, NCH), 6.72–6.76 [4 H, m, 4 *o*-CH_{Ar}(OCH_3)], 7.08–7.10 [2 H, m, 2 *o*-CH_{Ar}(CCH)], 7.18–7.20 [2 H, m, 2 *o*-CH_{Ar}(CS)] ppm; ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 20.28 (CH_3), 55.33 [*p*-($C_{Ar}OCH_3$)(CCH)], 55.40 [*p*-($C_{Ar}OCH_3$)(CS)], 57.81 (NCH_2), 84.67 (NCH), 114.14 [2 *m*-CH_{Ar}(CS)], 114.22 [2 *m*-CH_{Ar}(CCH)], 114.29 (C=CH_2), 126.42 (C_{Ar}CS), 126.57 (CHC=C), 129.74 (C_{Ar}CCH), 130.05 [2 *o*-CH_{Ar}(CCH)], 131.52 [2 *o*-CH_{Ar}(CS)], 134.21 (CHC=C), 139.66 (C=CH_2), 159.19 [*p*-C_{Ar}(CCH)], 160.28 [*p*-C_{Ar}(CS)], 189.64 (C=S) ppm; MS (ESI): m/z 436.1 ($M+Na^+$, 80%), 396.1 ($M–OH^+$, 100%); HRMS (ESI): Found 436.1013; Calc. for $C_{22}H_{23}NNaO_3S_2$ $[M+Na]^+$ 436.1017.

(*RS*)-3-(But-3-en-1-yl)-4-hydroxy-5,6-bis(4-methoxyphenyl)-3,4-dihydro-2*H*-1,3-thiazine-2-thione (2p): Following **GP A**, aldehyde (*EZ*)-**1d** (909 mg, 3.00 mmol), but-3-en-1-amine (321 mg, 4.50 mmol), CS_2 (684 mg, 9.00 mmol) and anhydrous Et_3N (153 mg, 1.50 mmol) were used. Column chromatography (DCM; R_f = 0.17) afforded the desired thiazinethione **2p** (698 mg, 56%) as a yellow oil; IR (ATR): $\tilde{\nu}$ 3292, 3073, 3002, 2932, 1639, 1603, 1506, 1291, 1246, 1173, 1125, 732 cm^{-1}; ^1H NMR (500.1 MHz, $CDCl_3$): δ 2.50–2.53 (2 H, m, $NCH_2C$$H_2$), 3.72 [3 H, s, *p*-($C_{Ar}OCH_3$)(CCH)], 3.73 [3 H, s, *p*-($C_{Ar}OCH_3$)(CS)], 4.05–4.06 (1 H, m, NCH_2), 4.46–4.48 (1 H, m, NCH_2), 4.53–4.58 (1 H, m, OH), 4.93–4.95 (1 H, m, CH=CH_2), 5.00–5.04 (1 H, m, CH=CH_2), 5.67 (1 H, s, NCH), 5.67–5.73 (1 H, m, CH=CH_2), 6.68–6.71 [4 H, m, 4 *o*-CH_{Ar}(OCH_3)], 7.09–7.10 [2 H, m, 2 *o*-CH_{Ar}(CCH)], 7.15–7.17 [2 H, m, 2 *o*-CH_{Ar}(CS)] ppm; ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 32.07 ($NCH_2C$$H_2$), 53.49 ($NCH_2$), 55.20 [*p*-($C_{Ar}OCH_3$)(CCH)], 55.24 [*p*-($C_{Ar}OCH_3$)(CS)], 86.42 (NCH), 113.83 [2 *m*-CH_{Ar}(CS)], 113.99 [2 *m*-

CH_{Ar}(CCH)], 117.84 (CH=CH_2), 125.98 (CHC=C), 126.34 (C_{Ar}CS), 129.66 (C_{Ar}CCH), 130.05 [2 *o*-CH_{Ar}(CCH)], 131.40 [2 *o*-CH_{Ar}(CS)], 133.81 (CHC=C), 134.24 (CH=CH_2), 158.86 [*p*-C_{Ar}(CCH)], 159.93 [*p*-C_{Ar}(CS)], 188.70 (C=S) ppm; MS (ESI): m/z 436.1 ($M+Na^+$, 40%), 396.1 ($M–OH^+$, 80%), 352.1 ($M–COS^+$, 100%); HRMS (ESI): Found 436.1017; Calc. for $C_{22}H_{23}NNaO_3S_2$ $[M+Na]^+$ 436.1017.

(*RS*)-4-Hydroxy-3-isopropyl-5,6-bis(4-methoxyphenyl)-3,4-dihydro-2*H*-1,3-thiazine-2-thione (2q): Following **GP A**, aldehyde (*EZ*)-**1d** (303 mg, 1.00 mmol), isopropylamine (89 mg, 1.50 mmol), CS_2 (228 mg, 3.00 mmol) and anhydrous Et_3N (51 mg, 0.50 mmol) were used. Column chromatography (DCM; R_f = 0.06) afforded the desired thiazinethione **2q** (242 mg, 60%) as an orange oil; IR (ATR): $\tilde{\nu}$ 3350, 3000, 2975, 2838, 1664, 1604, 1508, 1463, 1443, 1294, 1247, 1166, 1062, 1029, 938, 830, 818, 733 cm^{-1}; ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 1.09 (3 H, d, ^3J = 7.0 Hz, CHCH_3), 1.47 (3 H, d, ^3J = 7.0 Hz, CHCH_3), 3.75 (6 H, 2 s, 2 OCH_3), 5.75 (1 H, s, NCH), 5.83 (1 H, sept, ^3J = 7.0 Hz, CHCH$_3$), 6.71–6.75 [4 H, m, 2 *o*-$CH_{Ar}(OCH_3)$], 7.09–7.12 [2 H, m, 2 *o*-CH_{Ar}(CCH)], 7.17–7.20 [2 H, m, 2 *o*-CH_{Ar}(CS)] ppm; ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 20.52, 20.66 [CH(CH_3)$_2$], 52.21 [CH(CH_3)$_2$], 55.29, 55.34 (OCH_3), 79.65 (NCH), 114.11 [4 *o*-$CH_{Ar}(OCH_3)$], 126.27 (CHC=C), 126.98 (C_{Ar}CCH), 129.37 (C_{Ar}CS), 129.89 [2 *o*-CH_{Ar}(CCH)], 131.52 [*o*-CH_{Ar}(CS)], 133.93 (CHC=C), 159.07 [*p*-C_{Ar}(CCH)], 160.11 [*p*-C_{Ar}(CS)], 188.37 (C=S) ppm; MS (ESI): m/z 402.1 ($M+H^+$, 3%), 384.1 ($M–OH^+$, 10%), 340.1 ($M–COS^+$, 100%); HRMS (ESI): Found 402.1206; Calc. for $C_{21}H_{24}NO_3S_2$ $[M+H]^+$ 402.1198.

(*RS*)-4-Hydroxy-3-(2-methoxyethyl)-5,6-bis(4-methoxyphenyl)-3,4-dihydro-2*H*-1,3-thiazine-2-thione (2s): Following **GP A**, aldehyde (*EZ*)-**1d** (303 mg, 1.00 mmol), 2-methoxyethan1-amin (113 mg, 1.50 mmol), CS_2 (228 mg, 3.00 mmol) and anhydrous Et_3N (51 mg, 0.50 mmol) were used. Column chromatography (DCM; R_f = 0.26) afforded the desired thiazinethione **2s** (337 mg, 81%) as a yellow oil; IR (ATR): $\tilde{\nu}$ 3358, 2995, 2932, 2834, 1604, 1506, 1442, 1335, 1246, 1158, 1100,3 1027, 827 cm^{-1}; ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 3.46–3.52 (1 H, m, NCH_2), 3.50 (3 H, s, CH_2OCH_3), 3.56–3.59 (1 H, m, OCH_2), 3.76, 3.77 (6 H, 2 s, 2 $C_{Ar}OCH_3$), 4.27–4.32 (1 H, m, OCH_2), 5.10–5.14 (1 H, m, NCH_2), 5.40 (1 H, d, ^3J = 2.8 Hz, OH), 5.63 (1 H, d, ^3J = 2.8 Hz, NCH), 6.71–6.75 [4 H, m, 4 *o*-$CH_{Ar}(OCH_3)$], 7.11–7.14 [2 H, m, 2 *o*-CH_{Ar}(CCH)], 7.20–7.23 [2 H, m, 2 *o*-CH_{Ar}(CS)] ppm; ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 55.33, 55.36 ($C_{Ar}OCH_3$), 55.78 (NCH_2), 59.30 (CH_2OCH_3), 69.95 (OCH_2), 87.54 (NCH), 113.85, 114.05 [4 *o*-$CH_{Ar}(OCH_3)$], 125.19 (CHC=C), 126.74 (C_{Ar}CS), 130.28 [2 *o*-CH_{Ar}(CCH)], 130.38 (C_{Ar}CCH), 131.64 [*o*-CH_{Ar}(CS)], 134.41 (CHC=C), 158.92 [*p*-C_{Ar}(CCH)], 160.03 [*p*-C_{Ar}(CS)], 190.44 (C=S) ppm; MS (ESI): m/z 440.1 ($M+Na^+$, 30%), 400.1 ($M–OH^+$, 100%); HRMS (ESI): Found 440.0971; Calc. for $C_{21}H_{23}NNaO_4S_2$ $[M+Na]^+$ 440.0966.

(*RS*)-4-Hydroxy-3-(2-phenoxyethyl)-5,6-bis(4-methoxyphenyl)-3,4-dihydro-2*H*-1,3-thiazine-2-thione (2t): Following **GP A**, aldehyde (*EZ*)-**1d** (303 mg, 1.00 mmol), 2-phenoxyethan1-amin (206 mg, 1.50 mmol), CS_2 (228 mg, 3.00 mmol) and anhydrous Et_3N (51 mg, 0.50 mmol) were used. Column chromatography (DCM; R_f = 0.18) afforded the desired thiazinethione **2t** (311 mg, 65%) as a yellow oil; IR (ATR): $\tilde{\nu}$ 3410, 3037, 2951, 2934, 2836, 1601, 1506, 1494, 1292, 1244, 1163, 1029, 996, 908, 827, 729 cm^{-1}; ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 3.76, 3.77 (6 H, 2 s, 2 OCH_3), 4.21–4.29 (2 H, m, NCH_2, OCH_2), 4.63–4.67 (1 H, m, OCH_2), 4.88–4.93 (1 H, m, NCH_2), 4.53 (1 H, d, ^3J = 3.3 Hz, OH), 5.93 (1 H, d, ^3J = 3.3 Hz, NCH), 6.72–6.76 [4 H, m, 4 *o*-$CH_{Ar}(OCH_3)$], 6.78–6.80 [2 H, m, 2 *o*-$CH_{Ar}(OCH_2)$], 6.98–7.01 [1 H, m, *p*-$CH_{Ar}(OCH_2)$], 7.13–7.16 [2 H, m, 2 *o*-CH_{Ar}(CCH)], 7.20–7.23 [2 H, m, 2 *o*-CH_{Ar}(CS)], 7.25–7.29 [2 H, m, 2 *m*-$CH_{Ar}(OCH_2)$] ppm; ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 54.38 (NCH_2), 55.31 (OCH_3), 66.00 (OCH_2), 87.77 (NCH), 113.90, 114.05 [4 *o*-$CH_{Ar}(OCH_3)$], 114.55 [2 *o*-$CH_{Ar}(OCH_2)$], 122.08 [*p*-$CH_{Ar}(OCH_2)$], 125.59 (CHC=C), 126.49 (C_{Ar}CS), 129.81 [2 *m*-$CH_{Ar}(OCH_2)$], 130.05 (C_{Ar}CCH), 130.22 [2 *o*-CH_{Ar}(CCH)], 131.56 [*o*-CH_{Ar}(CS)], 134.19 (CHC=C), 157.47 ($C_{Ar}OCH_2$), 158.98 [*p*-C_{Ar}(CCH)], 160.05 [*p*-C_{Ar}(CS)], 190.21 (C=S) ppm; MS (ESI): m/z 502.0 ($M+Na^+$, 20%), 462.0 ($M–OH^+$, 40%), 318.1 ($M–COS^+$, 100%); HRMS (ESI): Found 502.1131; Calc. for $C_{26}H_{25}NNaO_4S_2$ $[M+Na]^+$ 502.1123.

(*RS*)-3-Benzyl-4-hydroxy-5,6-bis(4-methoxyphenyl)-3,4-dihydro-2*H*-1,3-thiazine-2-thione (2u): Following **GP A**, aldehyde (*EZ*)-**1d** (303 mg, 1.00 mmol), benzylamine (161 mg, 1.50 mmol), CS_2 (228 mg, 3.00 mmol) and anhydrous Et_3N (51 mg, 0.50 mmol) were used. Purification by twofold column chromatography (1. DCM; R_f = 0.09; 2. DCM/*n*-hexane/EtOAc 20:17:3; R_f = 0.42) afforded the desired thiazinethione **2u** (291 mg, 65%) as a red oil; IR (ATR): $\tilde{\nu}$ 3313, 3064, 3033, 2934, 1605, 1481, 1442, 1247, 797, 731, 699 cm^{-1}; ^1H NMR (500.1 MHz, $CDCl_3$): δ 3.71 [3 H, s, *p*-($C_{Ar}OCH_3$)(CCH)], 3.75 [3 H, s, *p*-($C_{Ar}OCH_3$)(CS)], 5.23 (1 H, d, ^2J = 15.3 Hz, NCH_2), 5.69 (1 H, s, NCH), 5.84 (1 H, d, ^2J = 15.3 Hz, NCH_2), 6.64–6.65 [2 H, m, 2 *m*-CH_{Ar}(CCH)], 6.72–6.74 [2 H, m, 2 *m*-CH_{Ar}(CS)], 6.98–6.99 [2 H, m, 2 *o*-CH_{Ar}(CCH)], 7.17–7.18 [2 H, m, 2 *o*-CH_{Ar}(CS)], 7.25–7.30 (3 H, m, 3 CH_{Ar}), 7.34–7.35 (2 H, m, CH_{Ar}) ppm; ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 55.24, 55.33 (OCH_3), 55.77 (NCH_2), 85.07 (NCH), 113.90 [2 *m*-CH_{Ar}(CCH)], 114.09 [2 *m*-CH_{Ar}(CS)], 126.22 (CH*C*=C), 126.35 (C_{Ar}CS), 128.04 [2 *o*-*C*H_{Ar}(CH_2)], 128.18 [*p*-*C*H_{Ar}(CH_2)], 128.99 [2 *m*-*C*H_{Ar}(CH_2)], 129.52 (C_{Ar}CCH), 129.99 [2 *o*-*C*H_{Ar}(CS)], 131.40 [2 *o*-*C*H_{Ar}(CCH)], 134.11 (CHC=*C*), 135.50 ($C_{Ar}CH_2$), 158.95 [*p*-C_{Ar}(CCH)], 160.07 [*p*-C_{Ar}(CS)], 190.12 (C=S) ppm; MS (ESI): m/z 472.1 ($M+Na^+$, 100%); HRMS (ESI): Found 472.1004; Calc. for $C_{25}H_{23}NNaO_3S_2$ $[M+Na]^+$ 472.1017.

(*RS*)-1,2-Diphenyl-6,7,12,12b-tetrahydro-4*H*-[1,3]thiazino[3',4':1,2]pyrido[3,4-*b*]indole-4-thione (3a): Following **GP A**, aldehyde (*EZ*)-**1a** (485 mg, 2.00 mmol), tryptamine (481 mg, 3.00 mmol), CS_2 (457 mg, 6.00 mmol) and anhydrous Et_3N (102 mg, 1.00 mmol) were used. Column chromatography (DCM/*n*-hexane 4:1; R_f = 0.43) afforded the desired thiazinethione **3a** (560 mg, 66%) as a yellow solid, mp 142–144 °C (from DCM/*n*-hexane); IR (ATR) $\tilde{\nu}$ 3312, 3046, 1574, 1483, 1454, 1414, 1345, 1270, 1247, 1230, 1131, 1054, 1030, 999, 950, 924, 753, 741, 696 cm^{-1}; ^1H NMR (500.1 MHz, $CDCl_3$): δ 2.89–2.92 (1 H, m, CH_2C_{Ar}), 3.32–3.36 (1 H, m, CH_2C_{Ar}), 3.82–3.88 (1 H, m, CH_2N), 5.43–5.47 (1 H, m, CH_2N), 6.12 (1 H, s, $NCHC_{Ar}$), 7.04–7.18 (13 H, m, 13 CH_{Ar}), 7.27 (1 H, s, NH), 7.44–7.46 (1 H, m, C*H*$_{Ar}$C$_{Ar}$NH) ppm; ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 20.07 (*C*H_2C_{Ar}), 50.02 (CH_2N), 63.61 (N*C*HC_{Ar}), 110.91 (CH_2C_{Ar}), 111.18 (CH_{Ar}), 118.46 (*C*$H_{Ar}C_{Ar}$NH), 120.05, 122.60 (2 CH_{Ar}), 126.02 (CH*C*=C), 126.60 (NCH*C*$_{Ar}$), 128.38, 128.60, 128.98, 129.06, 129.28 (9 CH_{Ar}), 129.85, 134.44, 134.61 (3 C_{Ar}), 135.90 (CHC=*C*), 136.43 ($CH_{Ar}C_{Ar}$NH), 190.37 (C=S) ppm; MS (ESI): m/z 447.1 ($M+Na^+$, 100%); HRMS (ESI): Found 447.0986; Calc. for $C_{26}H_{20}N_2NaS_2$ $[M+Na]^+$ 447.0966.

(*RS*)-1,2-Bis(4-methoxyphenyl)-6,7,12,12b-tetrahydro-4*H*-[1,3]thiazino[3',4':1,2]-pyrido[3,4-*b*]indole-4-thione (3b): Following **GP A**, aldehyde (*E*)-**1d** (606 mg, 2.00 mmol), tryptamine (481 mg, 3.00 mmol), CS_2 (457 mg, 6.00 mmol) and anhydrous Et_3N (102 mg, 1.00 mmol) were used. Column chromatography (DCM/*n*-hexane 3:2; R_f = 0.29) afforded the desired thiazinethione **3b** (486 mg, 50%) as a yellow solid, mp 133–135 °C (from DCM/*n*-hexane); IR (ATR): $\tilde{\nu}$ 3442, 2933, 2904, 2838, 1605, 1575, 1508, 1487, 1458, 1416, 1347, 1293, 1248, 1177, 1142, 1113, 1029, 1006, 957, 911, 831, 796, 650 cm^{-1}; ^1H NMR (500.1 MHz, $CDCl_3$): δ 2.89–2.93 (1 H, m, CH_2C_{Ar}), 3.38–3.40 (1 H, m, CH_2C_{Ar}), 3.75 (3 H, s, OCH_3), 3.76 (3 H, s, OCH_3), 3.84–3.89 (1 H, m, CH_2N), 5.50–5.54 (1 H, m, CH_2N), 6.16 (1 H, s, NCH), 6.71–6.76 [4 H, m, 4 *o*-C*H*$_{Ar}$(OCH_3)], 6.98–7.00 [2 H, m, 2 *o*-C*H*$_{Ar}$(CCH)], 7.06–7.11 (5 H, m, 5 CH_{Ar}), 7.26 (1 H, s, NH), 7.47–7.48 (1 H, m, CH_{Ar}) ppm; ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 20.07 (*C*H_2C_{Ar}), 50.14 (NCH_2), 55.35, 55.38 (2 OCH_3), 63.79 (NCH), 110.94 (CH_2C_{Ar}), 111.24 (CH_{Ar}), 114.11, 114.64 [4 *o*-*C*H_{Ar}(OCH_3)], 118.50, 120.11, 122.62, 124.94 (4 CH_{Ar}), 126.20, 127.03 (2 C_{Ar}), 128.77 (CH*C*=C), 130.33, 130.53 [4 *m*-*C*H_{Ar}(OCH_3), C_{Ar}], 133.01 (CHC=*C*), 135.85 (C_{Ar}), 159.35 [*p*-C_{Ar}(CCH)], 159.62 [*p*-C_{Ar}(CS)], 190.67 (C=S) ppm; MS (ESI): m/z 507.1 ($M+Na^+$, 100%); HRMS (ESI): Found 507.1183; Calc. for $C_{28}H_{24}N_2NaO_2S_2$ $[M+Na]^+$ 507.1177.

(*RS*)-1,2-Bis(4-methoxyphenyl)-11-methyl-6,7,12,12b-tetrahydro-4*H*-[1,3]thiazino[3',4':1,2]pyrido[3,4-*b*]indole-4-thione (3c): Following **GP A**, aldehyde (*EZ*)-**1d** (455 mg, 1.50 mmol), 7-methyltryptamine (261 mg, 2.25 mmol), CS_2 (342 mg, 4.50 mmol) and anhydrous Et_3N (77 mg, 0.75 mmol) were used. Purification by twofold column chromatography (1. DCM/*n*-hexane 3:2; 2.

DCM/EtOAc 9:1; R_f = 0.17) afforded the desired thiazinethione **3c** (359 mg, 48%) as a yellow oil; IR (ATR) $\tilde{\nu}$ 3441, 2931, 2837, 1604, 1506, 1410, 1292,3 1247, 1174, 1138, 1028, 911, 830, 726 cm^{-1}; ^1H NMR (500.1 MHz, $CDCl_3$): δ 2.13 (3 H, s, $C_{Ar}CH_3$), 2.87–2.92 (1 H, m, CH_2C_{Ar}), 3.34–3.40 (1 H, m, CH_2C_{Ar}), 3.75 (6 H, 2 s, 2 OCH_3), 3.83–3.89 (1 H, m, CH_2N), 5.53 (1 H, ddd, ^2J = 12.7 Hz, ^3J = 5.2 Hz, ^3J = 2.7 Hz, CH_2N), 6.18 (1 H, s, $NCHC_{Ar}$), 6.71–6.74 [2 H, m, 2 *m*-CH_{Ar}(CCH)], 6.76–6.79 [2 H, m, 2 *m*-CH_{Ar}(CS)], 6.90–6.91 [1 H, m, *o*-$CH_{Ar}(CH_3)$], 6.94–7.01 [1 H, m, *p*-$CH_{Ar}(CH_3)$], 6.99–7.02 [2 H, m, 2 *o*-CH_{Ar}(CCH)], 7.08–7.12 [2 H, m, 2 *o*-CH_{Ar}(CS)], 7.31–7.33 [1 H, m, *m*-$CH_{Ar}(CH_3)$] ppm; ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 16.14 ($C_{Ar}CH_3$), 20.25 (CH_2C_{Ar}), 50.11 (CH_2N), 55.35, 55.45 (2 OCH_3), 63.72 ($NCHC_{Ar}$), 111.31 (CH_2C_{Ar}), 114.09 [2 *m*-CH_{Ar}(CCH)], 114.67 [2 *m*-CH_{Ar}(CS)], 116.21 [*m*-$CH_{Ar}(CH_3)$], 120.17 ($C_{Ar}CH_3$), 120.29 [*p*-$CH_{Ar}(CH_3)$], 123.70 [*o*-$CH_{Ar}(CH_3)$], 124.96 (CHC=C), 125.55 [*m*-$C_{Ar}(CH_3)$], 126.93 (C_{Ar}CCH), 129.05 (C_{Ar}CS), 130.00 ($NCHC_{Ar}$), 130.30 [2 *o*-CH_{Ar}(CCH)], 130.64 [2 *o*-CH_{Ar}(CS)], 132.60 (CHC=*C*), 135.93 [*o*-$C_{Ar}(CH_3)$], 159.42 [*p*-C_{Ar}(CCH)], 159.60 [*p*-C_{Ar}(CS)], 190.32 (C=S) ppm; MS (ESI): m/z 521.1 ($M+Na^+$, 100%); HRMS (ESI): Found 521.1341; Calc. for $C_{29}H_{26}N_2O_2NaS_2$ $[M+Na]^+$ 521.1333.

(*RS*)-8-Methoxy-1,2-bis(4-methoxyphenyl)--6,7,12,12b-tetrahydro-4*H*-[1,3]thiazino[3',4':1,2]pyrido[3,4-*b*]indole-4-thione (3d): Following **GP A**, aldehyde (*E*)-**1d** (606 mg, 2.00 mmol), 4-methoxytryptamine (571 mg, 3.00 mmol), CS_2 (457 mg, 6.00 mmol) and anhydrous Et_3N (102 mg, 1.00 mmol) were used. Column chromatography (1. DCM/*n*-hexane 3:2; 2. DCM/EtOAc 9:1; R_f = 0.12) afforded the desired thiazinethione **3d** (618 mg, 60%) as a yellow solid, mp 144–145 °C (from DCM/*n*-hexane);; IR (ATR) $\tilde{\nu}$ 3440, 2997, 2952, 2933, 2909, 2835, 1603, 1506, 1484, 1438, 1414, 1291, 1246, 1174, 1137, 1026, 828, 794, 728 cm^{-1}; ^1H NMR (500.1 MHz, $CDCl_3$): δ 2.84–2.87 (1 H, m, CH_2C_{Ar}), 3.34–3.41 (1 H, m, CH_2C_{Ar}), 3.76 (6 H, 2 s, 2 $CH_{Ar}CH_{Ar}C_{Ar}OCH_3$), 3.84 (3 H, s, $C_{Ar}CH_{Ar}C_{Ar}OCH_3$), 3.86–3.89 (1 H, m, CH_2N), 5.51–5.55 (1 H, m, CH_2N), 6.15 (1 H, s, $NCHC_{Ar}$), 6.71–6.76 [4 H, m, 2 *m*-CH_{Ar}(CCH), 2 *m*-CH_{Ar}(CS)], 6.76–6.78 [1 H, m, *m*-CH_{Ar}(NH)], 6.90–6.90 [1 H, m, *m*-CH_{Ar}(NH)], 6.98–7.01 [2 H, m, 2 *o*-CH_{Ar}(CCH)], 6.99–7.01 [1 H, m, *o*-CH_{Ar}(NH)], 7.06–7.09 [1 H, m, *o*-CH_{Ar}(CS)], 7.15 (1 H, s, NH) ppm; ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 20.09 (CH_2C_{Ar}), 50.18 (CH_2N), 55.35, 55.38 (2 $CH_{Ar}CH_{Ar}C_{Ar}OCH_3$), 55.96 ($C_{Ar}CH_{Ar}C_{Ar}OCH_3$), 63.85 ($NCHC_{Ar}$), 100.26 [*m*-$CH_{Ar}$(NH)], 110.68 ($CH_2C_{Ar}$), 112.03 [*m*-$CH_{Ar}$(NH)], 112.69 [*o*-$CH_{Ar}$(NH)], 114.10, 114.61 [2 *m*-CH_{Ar}(CCH), 2 *m*-CH_{Ar}(CS)], 124.88, 126.64, 127.03 (3 C_{Ar}), 128.80 (CHC=C), 130.33 [2 *o*-CH_{Ar}(CCH)], 130.52 [2 *o*-CH_{Ar}(CS)], 130.89, 131.09 (2 C_{Ar}), 132.88 (CHC=*C*), 154.42 [*p*-C_{Ar}(NH)], 159.33 [*p*-C_{Ar}(CCH)], 159.60 [*p*-C_{Ar}(CS)], 190.62 (C=S) ppm; MS (ESI): m/z 537.1 ($M+Na^+$, 100%); HRMS (ESI): Found 537.1295; Calc. for $C_{29}H_{26}N_2O_3NaS_2$ $[M+Na]^+$ 537.1283.

(*RS*)-1,2-Bis(4-methoxyphenyl)-12-methyl-6,7,12,12b-tetrahydro-4*H*-[1,3]thiazino[3',4':1,2]pyrido[3,4-*b*]indole-4-thione (3e):
(*RS*)-4-Hydroxy-5,6-bis(4-methoxyphenyl)-3-(2-(1-methyl-1*H*-indol-3-yl)ethyl)-3,4-dihydro-2*H*-1,3-thiazine-2-thione (**2x**): Following **GP A**, aldehyde (*EZ*)-**1d** (455 mg, 1.50 mmol), 1-methyltryptamine (261 mg, 2.25 mmol), CS_2 (342 mg, 4.50 mmol) and anhydrous Et_3N (77 mg, 0.75 mmol) were used. Column chromatography (DCM/*n*-hexane/EtOAc 7:2:1; R_f = 0.36) afforded the thiazinethione **2x** (434 mg, 56%) as a brown solid, mp 155–157 °C (from DCM/*n*-hexane); IR (ATR): $\tilde{\nu}$ 3335, 2933, 2836, 1659, 1603, 1506, 1293, 1244, 1143, 1027, 930, 827, 735 cm^{-1}; ^1H NMR (500.1 MHz, $CDCl_3$): δ 3.22 (1 H, ddd, ^2J = 14.4 Hz, ^3J = 7.5 Hz, ^3J = 4.8 Hz, CH_2C_{Ar}), 3.35–3.41 (1 H, m, CH_2C_{Ar}), 3.54 (3 H, s, NCH_3), 3.62 (1 H, d, ^3J = 9.7 Hz, OH), 3.75 (6 H, 2 s, 2 $C_{Ar}OCH_3$), 4.26 (1 H, ddd, ^2J = 13.3 Hz, ^3J = 7.9 Hz, ^3J = 7.5 Hz, CH_2N), 4.78 (1 H, ddd, ^2J = 13.3 Hz, ^3J = 7.9 Hz, ^3J = 4.8 Hz, CH_2N), 5.40 (1 H, d, ^3J = 9.6 Hz, NCH), 6.59–6.62 [2 H, m, 2 *m*-CH_{Ar}(CCH)], 6.70–6.72 [2 H, m, 2 *m*-CH_{Ar}(CS)], 6.73–6.76 [2 H, m, 2 *o*-CH_{Ar}(CCH)], 7.10–7.13 [2 H, m, 2 *o*-CH_{Ar}(CS)], 6.81 (1 H, s, NCH_{Ar}), 7.09–7.11 (1 H, m, CH_{Ar}), 7.15–7.20 (2 H, m, 2 CH_{Ar}), 7.68–7.69 (1 H, m, CH_{Ar}) ppm; ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 23.36 (CH_2C_{Ar}),

32.56 (NCH_3), 55.29, 55.31 ($C_{Ar}OCH_3$), 55.58 (CH_2N), 87.14 (NCH), 109.42 (CH_{Ar}), 110.62 ($C_{Ar}CH_2$), 113.64 [2 *m*-CH_{Ar}(CCH)], 114.05 [2 *m*-CH_{Ar}(CS)], 119.03, 119.17, 121.76 (3 CH_{Ar}), 125.91 (CH*C*=C), 126.45 (C_{Ar}CS), 127.08 (NCH_{Ar}), 127.76 ($CH_2C_{Ar}C_{Ar}$), 129.30 (C_{Ar}CCH), 129.88 [2 *o*-CH_{Ar}(CCH)], 131.34 [2 *o*-CH_{Ar}(CS)], 133.46 (CHC=*C*), 136.97 (NC_{Ar}), 158.75 [*p*-C_{Ar}(CCH)], 159.99 [*p*-C_{Ar}(CS)], 188.52 (C=S) ppm. The 4-hydroxy-1,3-thiazine-2-thione **2x** (200 mg, 0.39 mmol) was kept in DCM for 3 d at r.t. Removing of the solvent on a rotary evaporator afforded the thiazinethione **3e** (194 mg, 100%) as a yellow oil; IR (ATR): $\tilde{\nu}$ 3035, 2931, 2835, 2835, 1603, 1505, 1406, 1291, 1246, 1175, 1027, 914, 815, 728, 638 cm^{-1}; ^1H NMR (500.1 MHz, $CDCl_3$): δ 2.94 (1 H, ddd, ^2J = 15.3 Hz, ^3J = 11.7 Hz, ^3J = 4.9 Hz, CH_2C_{Ar}), 3.21 (1 H, ddd, ^2J = 15.3 Hz, ^3J = 4.1 Hz, ^3J = 2.4 Hz, CH_2C_{Ar}), 3.65 (1 H, ddd, ^2J = 13.2 Hz, ^3J = 11.7 Hz, ^3J = 4.1 Hz, CH_2N), 5.05 (1 H, ddd, ^2J = 13.2 Hz, ^3J = 4.9 Hz, ^3J = 2.4 Hz, CH_2N), 3.39 (3 H, s, NCH_3), 3.57 [3 H, s, *p*-$C_{Ar}OCH_3$(CCH)], 3.74 [3 H, s, *p*-$C_{Ar}OCH_3$(CCH)], 5.56 ($NCHC_{Ar}$), 6.38–6.40 [2 H, m, 2 *m*-CH_{Ar}(CCH)], 6.62–6.65 [2 H, m, 2 *m*-CH_{Ar}(CS)], 6.69–6.72 [2 H, m, 2 *m*-CH_{Ar}(CS)], 7.00–7.03 [2 H, m, 2 *o*-CH_{Ar}(CS)], 7.10–7.13 [2 H, m, *o*-CH_{Ar}(N), *p*-CH_{Ar}(N)], 7.15–7.19 [2 H, m, *m*-CH_{Ar}(N)], 7.26 (1 H, s, NH), 7.47–7.48 (1 H, m, CH_{Ar}), 7.52–7.54 [2 H, m, *m*-CH_{Ar}(N)] ppm; ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 20.45 (CH_2C_{Ar}), 30.22 (NCH_3), 49.91 (NCH_2), 55.08 [*p*-$C_{Ar}OCH_3$(CCH)], 55.34 [*p*-$C_{Ar}OCH_3$(CS)], 62.83 (N*C*HC$_{Ar}$), 109.29 [*o*-CH_{Ar}(N)], 109.92 (CH_2C_{Ar}), 113.29 [2 *m*-CH_{Ar}(CCH)], 113.83 [2 *m*-CH_{Ar}(CS)], 118.55 [*m*-CH_{Ar}(N)], 119.63 [*p*-CH_{Ar}(N)], 122.09 [*m*-CH_{Ar}(N)], 125.27 [*o*-CH_{Ar}(N)], 127.33 (C_{Ar}CCH), 127.79 (C_{Ar}CS), 130.05 ($NCHC_{Ar}$), 130.58 [2 *o*-CH_{Ar}(CS)], 130.82 [2 *o*-CH_{Ar}(CCH)], 131.10 (CH*C*=C), 137.48 (NC_{Ar}), 138.04 (CHC=*C*), 158.64 [*p*-C_{Ar}(CCH)], 159.46 [*p*-C_{Ar}(CS)], 192.64 (C=S) ppm; MS (ESI): m/z 499.1 (M^+, 30%); HRMS (ESI): Found 521.1339; Calc. for $C_{29}H_{26}N_2NaO_2S_2$ $[M+Na]^+$ 521.1333.

General Procedure (GP B)

Under argon atmosphere the respective 4-hydroxy-1,3-thiazine-2-thione (1.0 equiv.) was dissolved in anhydrous DCM (5 mL per mmol thiazinethione). Afterwards $InCl_3$ (1.0 equiv.) was added to the solution. After stirring overnight at r.t. the reaction was quenched with saturated aqueous $NaHCO_3$ solution (10 mL per mmol thiazinethione). The layers were seperated and the aqueous phase was extracted with DCM (3 x 10 mL per mmol thiazinethione). The combined organic phases were dried ($MgSO_4$) and the solvent was removed on a rotary evaporator. In a final step the crude product was purified by column chromatography on silica gel.

(4a*R,6*R**)- and (4a*R**,6*S**)-6-Chloro-3,4-diphenyl-4a,5,7,8-tetrahydro-1*H*,6*H*-pyrido[1,2-c][1,3]thiazine-1-thione (4a):** Following **GP B**, thiazinethione **2c** (629 mg, 1.78 mmol) and $InCl_3$ (393 mg, 1.78 mmol) were used. After column chromatography (*n*-hexane/EtOAc 4:1), the two diastereomers were isolated in 62% overall yield; dr = 72:28 (determined from isolated yields); MS (ESI): m/z 394.1 ($M+Na^+$, 100%); HRMS (ESI): Found 394.0479; Calc. for $C_{20}H_{18}ClNNaS_2$ $[M+Na]^+$ 394.0467.

Major Diastereomer

The column chromatography (*n*-hexane/EtOAc 4:1; R_f = 0.37) afforded the major diastereomer of the desired pyridothiazinethione (295 mg, 45%) as a yellow oil; IR (ATR): $\tilde{\nu}$ 3061, 3024, 2925, 2853, 1598, 1441, 1431, 1276, 752, 729, 696 cm^{-1}; ^1H NMR (500.1 MHz, $CDCl_3$): δ 1.97–2.33 (4 H, m, NCH_2CH_2, $NCHCH_2$), 3.04–3.09 (1 H, m, NCH_2), 4.05–4.12 (1 H, m, CClH), 4.62 (1 H, dd, ^3J = 6.1 Hz, ^3J = 8.3 Hz, NCH), 5.81 (1 H, ddd, ^2J = 2.6 Hz, ^3J = 4.1 Hz, ^3J = 13.3 Hz, NCH_2), 7.03–7.07 (4 H, m, 4 CH_{Ar}), 7.13–7.16 (3 H, m, 3 CH_{Ar}), 7.19–7.21 (3 H, m, 3 CH_{Ar}) ppm; ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 35.13 (NCH_2CH_2), 39.98 ($NCHCH_2$), 50.61 (NCH_2), 55.70 (CCl), 66.53 (NCH), 126.88 (CH*C*=C), 128.00 (*p*-CH_{Ar}), 128.48 (2 CH_{Ar}), 128.53 (*p*-CH_{Ar}), 128.75, 128.88, 129.32 (6 CH_{Ar}), 130.79 (C_{Ar}CCH), 134.32 (C_{Ar}CS), 137.06 (CHC=*C*), 189.28 (C=S) ppm.

Minor Diastereomer

The column chromatography (*n*-hexane/EtOAc 4:1; R_f = 0.24) afforded the minor diastereomer of the desired pyridothiazinethione (115 mg, 17%) as a yellow oil; IR (ATR): $\tilde{\nu}$ 3002, 2932, 2836, 1604, 1444, 1427, 1246, 763, 728, 649 cm^{-1}; ^1H NMR (500.1 MHz, $CDCl_3$): δ 1.92–2.19 (2 H, m, NCH_2CH_2), 2.21–2.28 (2 H, m, $NCHCH_2$), 2.70–2.76 (1 H, m, NCH_2), 3.92–3.97 (1 H, m, CClH), 4.39 (1 H, dd, ^3J = 2.1 Hz, ^3J = 11.6 Hz, NCH), 4.86 (1 H, ddd, ^2J = 13.6 Hz, ^3J = 2.2 Hz, ^3J = 4.6 Hz, NCH_2), 7.03–7.06 (4 H, m, 4 CH_{Ar}), 7.15–7.16 (3 H, m, 3 CH_{Ar}), 7.19–7.20 (3 H, m, 3 CH_{Ar}) ppm; ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 35.74 (NCH_2CH_2), 39.94 ($NCHCH_2$), 44.93 (NCH_2), 55.92 (CCl), 65.41 (NCH), 127.56 (CHC=C), 127.86, 128.36 (*p*-CH_{Ar}), 128.44, 128.69, 128.98, 129.66 (8 CH_{Ar}), 129.86 (C_{Ar}CCH), 136.19 (C_{Ar}CS), 137.65 (CHC=*C*), 164.07 (C=S) ppm.

(4a*R,6*R**)- and (4a*R**,6*S**)-6-Chloro-3,4-bis(4-methoxyphenyl)-4a,5,7,8-tetrahydro-1*H*,6*H*-pyrido[1,2-c][1,3]thiazine-1-thione (4b):** Following **GP B**, thiazinethione **2p** (500 mg, 1.21 mmol) and $InCl_3$ (267 mg, 1.21 mmol) were used. After column chromatography (*n*-hexane/EtOAc 3:1), the two diastereomers were isolated in 31% overall yield; dr = 64:36 (determined from isolated yields); MS (ESI): m/z 454.1 ($M+Na^+$, 100%); HRMS (ESI): Found 442.0862; Calc. for $C_{22}H_{23}ClNO_2S_2$ $[M+H]^+$ 432.0859.

Major Diastereomer

The column chromatography (*n*-hexane/EtOAc 3:1; R_f = 0.31) afforded the major diastereomer of the desired pyridothiazinethione (105 mg, 20%) as a yellow oil; IR (ATR): $\tilde{\nu}$ 3058, 3027, 2929, 2855, 1599, 1444, 1433, 1241, 754, 731, 698 cm^{-1}; ^1H NMR (500.1 MHz, $CDCl_3$): δ 2.16–2.30 (4 H, m, $NCHCH_2$, NCH_2CH_2), 3.01–3.07 (1 H, m, NCH_2), 3.72 [3 H, s, *p*-($C_{Ar}OCH_3$)(CCH)], 3.75 [3 H, s, *p*-($C_{Ar}OCH_3$)(CS)], 4.04–4.11 (1 H, m, CClH), 4.54 (1 H, dd, ^3J = 4.3 Hz, ^3J = 9.5 Hz, NCH), 5.78 (1 H, ddd, ^2J = 13.3 Hz, ^3J = 2.5 Hz, ^3J = 4.2 Hz, NCH_2), 6.67–6.68 [2 H, m, 2 *m*-CH(CCH)], 6.73–6.75 [2 H, m, 2 *m*-CH(CS)], 6.95–6.97 [4 H, m, 4 *m*-CH(OCH_3)] ppm; ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 35.15 (NCH_2CH_2), 40.04 ($NCHCH_2$), 50.68 (NCH_2), 55.28 (OCH_3), 55.33 (OCH_3), 55.83 (CCl), 66.77 (NCH), 113.98 [2 *m*-CH(CCH)], 114.26 [2 *m*-CH(CS)], 125.85 (CHC=C), 126.78 (C_{Ar}CCH), 129.47 (C_{Ar}CS), 129.89 (CHC=*C*), 130.24 [2 *o*-CH(CS)], 130.48 [2 *o*-CH(CCH)], 159.14 [*p*-C_{Ar}(CS)], 159.55 [*p*-C_{Ar}(CCH)], 189.78 (C=S) ppm.

Minor Diastereomer

The column chromatography (*n*-hexane/EtOAc 3:1; R_f = 0.19) afforded the minor diastereomer of the desired pyridothiazinethione (58 mg, 11%) as a yellow oil; IR (ATR): $\tilde{\nu}$ 3057, 3024, 2963, 2857, 1600, 1445, 1428, 1232, 755, 731, 697 cm^{-1}; ^1H NMR (500.1 MHz, $CDCl_3$): δ 1.91–1.96 (2 H, m, $NCHCH_2$), 2.11–2.18 (1 H, m, NCH_2CH_2), 2.20–2.27 (1 H, m, NCH_2CH_2), 2.68–2.74 (1 H, m, NCH_2), 3.73 [3 H, s, *p*-($C_{Ar}OCH_3$)(CS)], 3.75 [3 H, s, *p*-($C_{Ar}OCH_3$)(CCH)], 3.91–3.98 (1 H, m, CClH), 4.32 (1 H, dd, ^3J = 2.1 Hz, ^3J = 11.5 Hz, NCH), 4.83 (1 H, ddd, ^2J = 13.6 Hz, ^3J = 2.2 Hz, ^3J = 4.5 Hz, NCH_2), 6.67–6.69 [2 H, m, 2 *m*-CH(CS)], 6.73–6.74 [2 H, m, 2 *m*-CH(CCH)], 6.95–6.98 [4 H, m, 4 *m*-CH(OCH_3)] ppm; ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 35.74 (NCH_2CH_2), 39.97 ($NCHCH_2$), 44.90 (NCH_2), 55.30 (OCH_3), 55.34 (OCH_3), 56.05 (CCl), 65.51 (NCH), 113.90 [2 *m*-CH(CS)], 114.18 [2 *m*-CH(CCH)], 126.60 (CHC=C), 128.72 (CHC=*C*), 128.78 (C_{Ar}CCH), 129.99 (C_{Ar}CS), 130.27 [2 *o*-CH(CS)], 130.78 [2 *o*-CH(CCH)], 159.03 [*p*-C_{Ar}(CCH)], 159.37 [*p*-C_{Ar}(CS)], 164.49 (C=S) ppm.

General Procedure (GP C)

Under argon atmosphere 5 mol% $InCl_3$ was dissolved in anhydrous DCM (6 mL per mmol thiazinethione). Afterwards the respective 4-hydroxy-1,3-thiazine-2-thione (1.0 equiv.), dissolved in anhydrous DCM (9 mL per mmol thiazinethione), was added to the solution. Next, the respective nucleophile (2.0 equiv.) was added to the reaction mixture. After stirring for 10 hours at r.t. the reaction was quenched with saturated aqueous $NaHCO_3$ solution (30 mL per mmol thiazinethione). The layers were seperated and the aqueous phase was extracted with DCM (3 x 15 mL per mmol thiazinethione). The combined organic phases were dried ($MgSO_4$) and the solvent

was removed on a rotary evaporator. In a final step the crude product was purified by column chromatography on silica gel.

(*RS*)-3,4-Diallyl-5,6-diphenyl-3,4-dihydro-2*H*-1,3-thiazine-2-thione (5a): Following **GP C**, thiazinethione **2a** (200 mg, 0.59 mmol), $InCl_3$ (7 mg; 30 µmol) and allyltrimethylsilane (135 mg, 1.18 mmol) were used. Column chromatography (DCM; R_f = 0.83) afforded the desired dialkene **5a** (206 mg, 97%) as a yellow oil; IR (ATR): $\tilde{\nu}$ 3079, 3052, 3018, 2979, 2931, 2909, 2856, 1473, 1461, 1440, 1412, 1332, 1232, 1148, 1134, 1098, 1014, 998, 983, 916, 752, 694 cm^{-1}; ^1H NMR (500.1 MHz, $CDCl_3$): δ 2.75–2.81 (1 H, m, NCHCH_2), 3.00–3.06 (1 H, m, NCHCH_2), 3.95–3.99 (1 H, m, NCH_2), 4.67–4.70 (1 H, m, NCH), 5.19–5.28 (4 H, m, 2 CH=CH_2), 5.70 (1 H, dddd, ^2J = 15.4 Hz, ^3J = 4.5 Hz, ^4J = 2.3 Hz, ^4J = 1.6 Hz, NCH_2), 5.83–5.88 (2 H, m, 2 CH=CH_2), 7.03–7.05 (2 H, m, 2 CH_{Ar}), 7.14–7.21 (8 H, m, 8 CH_{Ar}) ppm; ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 34.43 (NCHCH$_2$), 56.98 (NCH_2), 67.22 (NCH), 119.06 (NCH_2CH=CH$_2$), 120.08 (CHCH$_2$CH=CH$_2$), 127.61, 128.48, 128.56, 129.03 (8 CH_{Ar}), 129.11 (CHC=C), 129.55 (2 CH_{Ar}), 130.94 (NCH_2CH), 132.82 (CHCH$_2C$H=CH$_2$), 133.78 (CHC=C), 135.00, 138.15 (2 C_{Ar}), 189.29 (C=S) ppm; MS (ESI): m/z 386.1 (M+Na^+, 100%); HRMS (ESI): Found 386.1015; Calc. for $C_{22}H_{21}NNaS_2$ $[M+Na]^+$ 386.1013.

(*RS*)-4-Allyl-3-(2-methylallyl)-5,6-diphenyl-3,4-dihydro-2*H*-1,3-thiazine-2-thione (5b): Following **GP C**, thiazinethione **2b** (120 mg, 0.34 mmol), $InCl_3$ (4 mg; 17 µmol) and allyltrimethylsilane (78 mg, 0.68 mmol) were used. Column chromatography (*n*-hexane/DCM 1:1; R_f = 0.53) afforded the desired dialkene **5b** (93 mg, 74%) as a yellow oil; IR (ATR): $\tilde{\nu}$ 3077, 3056, 3022, 2975, 2931, 2914, 1476, 1442, 1414, 1340, 1280, 1220, 1163, 1147, 115, 1029, 999, 976, 757, 695 cm^{-1}; ^1H NMR (499.9 MHz, $CDCl_3$): δ 1.71 (3 H, s, CH_3), 2.71–2.77 (1 H, m, NCHCH_2), 3.04–3.10 (1 H, m, CHCH_2), 3.75 (1 H, d, ^2J = 15.3 Hz, NCH_2), 4.64–4.67 (1 H, m, NCH), 4.89–4.91 (1 H, m, C=CH_2), 4.96 (1 H, d, ^2J = 0.8 Hz, C=CH_2), 5.20–5.22 (1 H, m, CH=CH_2), 5.27–5.28 (1 H, m, CH=CH_2), 5.83–5.90 (2 H, m, CH=CH_2, NCH_2), 7.03–7.04 (2 H, m, 2 CH_{Ar}), 7.15–7.20 (8 H, m, 8 CH_{Ar}) ppm; ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 20.16 (CH_3), 34.31 (NCHCH$_2$), 59.80 (NCH_2), 66.77 (NCH), 114.34 (C=CH$_2$), 120.09 (CH=CH$_2$), 127.64, 128.53, 128.59, 129.04 (8 CH_{Ar}), 129.48 (CHC=C), 129.61 (2 CH_{Ar}), 132.91 (CH=CH$_2$), 133.78 (CHC=C), 135.14, 138.32 (2 C_{Ar}), 139.15 (C=CH$_2$), 189.80 (C=S) ppm; MS (ESI): m/z 378.1 (M+Na^+, 100%); HRMS (ESI): Found 378.1349; Calc. for $C_{23}H_{24}NS_2$ $[M+Na]^+$ 378.1350.

(*RS*)-3,4-Diallyl-5,6-bis(4-methoxyphenyl)-3,4-dihydro-2*H*-1,3-thiazine-2-thione (5c): Following **GP C**, thiazinethione **2m** (150 mg, 0.38 mmol), $InCl_3$ (4 mg; 19 µmol) and allyltrimethylsilane (87 mg, 0.76 mmol) were used. Column chromatography (*n*-hexane/EtOAc 9:1; R_f = 0.31) afforded the desired dialkene **5c** (127 mg, 79%) as a yellow oil; IR (ATR): $\tilde{\nu}$ 3074, 3001, 2956, 2932, 2835, 1603, 1506, 1479, 1439, 1414, 1338, 1291, 1244, 1175, 1161, 1131, 1111, 1029, 994, 927, 793, 685 cm^{-1}; ^1H NMR (500.1 MHz, $CDCl_3$): δ 2.75–2.80 (1 H, m, NCHCH_2), 2.98–3.02 (1 H, m, NCHCH_2), 3.75 (3 H, s, OCH_3), 3.76 (3 H, s, OCH_3), 3.94–3.98 (1 H, m, NCH_2), 4.60–4.63 (1 H, m, NCH), 5.19–5.26 (4 H, m, 2 CH=CH_2), 5.62–5.66 (1 H, m, NCH_2), 5.75–5.90 (2 H, m, 2 CH=CH_2), 6.69–6.74 [4 H, m, 4 *o*-CH_{Ar}(OCH_3)], 6.95–6.98 [2 H, m, 2 *o*-CH_{Ar}(CCH)], 7.09–7.12 [2 H, m, 2 *o*-CH_{Ar}(CS)] ppm; ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 34.45 (NCHCH$_2$), 55.29 [*p*-($C_{Ar}OCH_3$)(CCH)], 55.35 [*p*-($C_{Ar}OCH_3$)(CS)], 57.12 (NCH_2), 67.40 (NCH), 113.94 [2 *m*-CH_{Ar}(CS)], 114.03 [2 *m*-CH_{Ar}(CCH)], 119.00 (NCH_2CH=CH$_2$), 120.01 (CHCH$_2$CH=CH$_2$), 127.49 (C_{Ar}CS, CHC=C), 130.29 [2 *o*-CH_{Ar}(CCH)], 130.75 (C_{Ar}CCH), 131.04 (NCH_2CH), 131.08 [2 *o*-CH_{Ar}(CS)], 132.69 (CHC=C), 133.15 (CHCH$_2C$H=CH$_2$), 158.79 [*p*-C_{Ar}(CCH)], 159.71 [*p*-C_{Ar}(CS)], 189.44 (C=S) ppm; MS (ESI): m/z 424.1 (M+Na^+, 100%); HRMS (ESI): Found 424.1392; Calc. for $C_{24}H_{26}NO_2S_2$ $[M+Na]^+$ 424.1405.

(*RS*)-4-Allyl-5,6-bis(4-methoxyphenyl)-3-(2-methylallyl)-3,4-dihydro-2*H*-1,3-thiazine-2-thione (5d): Following **GP C**, thiazinethione **2o** (150 mg, 0.36 mmol), $InCl_3$ (4 mg; 18 µmol) and allyltrimethylsilane (82 mg, 0.72 mmol) were used. Column chromatography (DCM; R_f = 0.68) afforded the desired dialkene **5d** (130 mg, 83%) as a yellow oil; IR (ATR): $\tilde{\nu}$ 2933, 2836, 1604, 1506, 1478, 1439,

1413, 1340, 1291, 1245, 1175, 1163, 1147, 1112, 1029, 977, 953, 793, 647 cm^{-1}; ^1H NMR (499.9 MHz, $CDCl_3$): δ 1.67 (3 H, s, CCH_3), 2.70–2.76 (1 H, m, NCHCH_2), 3.02–3.08 (1 H, m, NCHCH_2), 3.73 (1 H, d, ^2J = 15.3 Hz, NCH_2), 3.75 (3 H, s, OCH_3), 3.76 (3 H, s, OCH_3), 4.58–4.61 (1 H, m, NCH), 4.85–4.86 (1 H, m, C=CH_2), 4.91 (1 H, d, ^2J = 0.8 Hz, C=CH_2), 5.19–5.21 (1 H, m, CH=CH_2), 5.23–5.27 (1 H, m, CH=CH_2), 5.81 (1 H, d, ^2J = 15.3 Hz, NCH_2), 5.84–5.91 (1 H, m, CH=CH_2), 6.69–6.73 [4 H, m, 4 *o*-CH_{Ar}(OCH_3)], 6.95–6.97 [2 H, m, 2 *o*-CH_{Ar}(CCH)], 7.09–7.11 [2 H, m, 2 *o*-CH_{Ar}(CS)] ppm; ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 20.16 (CCH_3), 34.29 (NCHCH_2), 55.28 [*p*-($C_{Ar}OCH_3$)(CCH)], 55.36 [*p*-($C_{Ar}OCH_3$)(CS)], 59.90 (NCH_2), 66.88 (NCH), 114.00 [2 *m*-CH_{Ar}(CS)], 114.07 [2 *m*-CH_{Ar}(CCH)], 114.31 (C=CH_2), 119.97 (CH=CH_2), 127.60 (CHC=C), 127.88 (C_{Ar}CS) 130.24 [2 *o*-CH_{Ar}(CCH)], 130.90 (C_{Ar}CCH), 131.08 [2 *o*-CH_{Ar}(CS)], 132.60 (CHC=*C*), 133.19 (*C*H=CH_2), 139.21 (*C*=CH_2), 158.85 [*p*-C_{Ar}(CCH)], 159.76 [*p*-C_{Ar}(CS)], 189.91 (C=S) ppm; MS (ESI): m/z 460.1 ($M+Na^+$, 100%); HRMS (ESI): Found 460.1365; Calc. for $C_{25}H_{27}NNaO_2S_2$ $[M+Na]^+$ 460.1381.

(*RS*)-4-(Allylthio)-3-(2-methylallyl)-5,6-diphenyl-3,4-dihydro-2*H*-1,3-thiazine-2-thione (5e): Following **GP C**, thiazinethione **2b** (120 mg, 0.34 mmol), $InCl_3$ (4 mg; 17 µmol) and allyl mercaptan (50 mg, 0.68 mmol) were used. Column chromatography (*n*-hexane/DCM 7:3; R_f = 0.30) afforded the desired dialkene **5e** (82 mg, 59%) as a yellow oil; IR (ATR): $\tilde{\nu}$ 3079, 3055, 3021, 2975, 2914, 1597, 1575, 1462, 1442, 1427, 1377, 1326, 1271, 1223, 1141, 1087, 1054, 1028, 994, 917, 757, 695 cm^{-1}; ^1H NMR (499.9 MHz, $CDCl_3$): δ 1.72 (3 H, s, CH_3), 3.30–3.34 (1 H, m, SCH_2), 3.44–3.49 (1 H, m, SCH_2), 3.86 (1 H, d, ^2J = 15.6 Hz, NCH_2), 4.88–4.90 (1 H, m, C=CH_2), 4.95–4.97 (1 H, m, C=CH_2), 5.12–5.14 (1 H, m, CH=CH_2), 5.15–5.16 (1 H, m, CH=CH_2), 5.51 (1 H, s, NCH), 5.84–5.92 (1 H, m, CH=CH_2), 5.93 (1 H, d, ^2J = 15.7 Hz, NCH_2), 7.15–7.22 (10 H, m, 10 CH_{Ar}) ppm; ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 20.14 (CH_3), 34.40 (SCH_2), 57.93 (NCH_2), 68.77 (NCH), 114.29 (C=*C*H_2), 118.66 (CH=*C*H_2), 126.85 (CH*C*=C), 128.04, 128.56, 128.61, 128.91, 129.04, 129.66 (10 CH_{Ar}), 133.69 (*C*H=CH_2), 134.48 (CH_{Ar}), 135.66 (CHC=*C*), 137.42 (C_{Ar}), 138.89 (*C*=CH_2), 191.53 (C=S) ppm; MS (ESI): m/z 432.1 ($M+Na^+$, 100%); HRMS (ESI): Found 432.0888; Calc. for $C_{23}H_{23}NNaS_3$ $[M+Na]^+$ 432.0890.

(*RS*)-4-(Allyloxy)-5,6-bis(4-methoxyphenyl)-3-(2-methylallyl)-3,4-dihydro-2*H*-1,3-thiazine-2-thione (5f): Following **GP C**, thiazinethione **2o** (150 mg, 0.36 mmol), $InCl_3$ (4 mg; 18 µmol) and allyl alcohol (42 mg, 0.72 mmol) were used. Column chromatography (*n*-hexane/MTBE 1:1; R_f = 0.57) afforded the desired dialkene **5f** (49 mg, 31%) as a yellow oil; IR (ATR): $\tilde{\nu}$ 3081, 3003, 2957, 2932, 2838, 1606, 1508, 1466, 1442, 1417, 1332, 1293, 1247, 1176, 1161, 1148, 1116, 1030, 980, 932, 798, 632 cm^{-1}; ^1H NMR (499.9 MHz, $CDCl_3$): δ 1.66 (3 H, s, CCH_3), 3.74 (3 H, s, OCH_3), 3.75 (3 H, s, OCH_3), 3.98 (1 H, d, ^2J = 15.6 Hz, NCH_2), 4.12–4.16 (1 H, m, OCH_2), 4.29–4.32 (1 H, m, OCH_2), 4.78–4.79 (1 H, m, C=CH_2), 4.86–4.87 (1 H, m, C=CH_2), 5.26–5.28 (1 H, m, CH=CH_2), 5.35–5.39 (1 H, m, CH=CH_2), 5.58 (1 H, s, NCH), 5.89 (1 H, d, ^2J = 15.7 Hz, NCH_2), 5.96–6.02 (1 H, m, CH=CH_2), 6.70–6.74 [4 H, m, 4 *o*-CH_{Ar}(OCH_3)], 7.02–7.05 [2 H, m, 2 *o*-CH_{Ar}(CCH)], 7.16–7.19 [2 H, m, 2 *o*-CH_{Ar}(CS)] ppm; ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 20.12 (CCH_3), 55.23 [*p*-($C_{Ar}OCH_3$)(CCH)], 55.30 [*p*-($C_{Ar}OCH_3$)(CS)], 58.14 (NCH_2), 67.38 (OCH_2), 88.67 (NCH), 113.65 (C=*C*H_2), 113.96 [2 *m*-CH_{Ar}(CS)], 114.01 [2 *m*-CH_{Ar}(CCH)], 118.25 (CH=*C*H_2), 123.65 (CH*C*=C), 126.54 (C_{Ar}CS), 130.08 (C_{Ar}CCH), 130.11 [2 *o*-CH_{Ar}(CCH)], 131.30 [2 *o*-CH_{Ar}(CS)], 133.77 (*C*H=CH_2), 136.04 (CHC=*C*), 138.84 (*C*=CH_2), 158.91 [*p*-C_{Ar}(CCH)], 160.02 [*p*-C_{Ar}(CS)], 191.54 (C=S) ppm; MS (ESI): m/z 476.1 ($M+Na^+$, 100%); HRMS (ESI): Found 476.1328; Calc. for $C_{25}H_{27}NNaO_3S_2$ $[M+Na]^+$ 476.1328.

General Procedure (GP D)

Under argon atmosphere the respective diene (1.0 equiv.) and Ru-catalyst **A** (5 mol%) were dissolved in anhydrous toluene (20 mL per mmol diene). Afterwards the mixture was slowly heated to 70 °C until the reaction was finished, as shown by TLC. The mixture was then stirred over night at r.t., and then the solvent was removed on a rotary evaporator. In a final step the crude product was purified by column chromatography on silica gel.

(*RS*)-3,4-Diphenyl-4a,5-dihydro-1*H*,8*H*-pyrido[1,2-*c*][1,3]thiazine-1-thione (6a): Following **GP D**, dialkene **5a** (100 mg, 0.28 mmol) and Ru-catalyst **A** (13 mg; 14 µmol) were used. A twofold column chromatography (1. *n*-hexane/EtOAc 20:1, 2. *n*-hexane/DCM 1:1; R_f = 0.38) afforded the desired pyridothiazinethione **6a** (51 mg, 54%) as a colorless solid, mp 175–177 °C (from DCM/*n*-hexane); IR (ATR): $\tilde{\nu}$ 3075, 3055, 3038, 3021, 2959, 2922, 2879, 2853, 1487, 1441, 1423, 1353, 1327, 1264, 1195, 1137, 1071, 1026, 1000, 977, 946, 922, 752, 690 cm^{-1}; ^1H NMR (499.9 MHz, $CDCl_3$): δ 2.28–2.33 (1 H, m, NCHCH_2), 2.89–2.96 (1 H, m, NCHCH_2), 3.87 (1 H, ddd, ^2J = 17.6 Hz, ^3J = 4.1 Hz, ^4J = 1.8 Hz, NCH_2), 4.87 (dd, ^3J = 11.5 Hz, ^3J = 3.3 Hz, NCH), 5.78–5.86 (2 H, m, C*H*=C*H*), 6.16–6.21 (1 H, m, NCH_2), 7.04–7.11 (4 H, m, 4 CH_{Ar}), 7.14–7.21 (6 H, m, 6 CH_{Ar}) ppm; ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 30.59 (NCH*C*H_2), 50.51 (NCH_2), 64.57 (NCH), 125.23, 126.28 (*C*H=*C*H), 127.19 (CH*C*=C), 127.83, 128.51, 128.53, 129.22, 129.27 (10 CH_{Ar}), 130.68, 134.86 (2 C_{Ar}), 137.92 (CHC=*C*), 188.79 (C=S) ppm; MS (ESI): m/z 358.1 ($M+Na^+$, 100%); HRMS (ESI): Found 358.0699; Calc. for $C_{20}H_{17}NNaS_2$ $[M+Na]^+$ 358.0700.

(*RS*)-7-Methyl-3,4-diphenyl-4a,5-dihydro-1*H*,8*H*-pyrido[1,2-*c*][1,3]thiazine-1-thione (6b): Following **GP D**, dialkene **5b** (83 mg, 0.22 mmol) and Ru-catalyst **A** (10 mg; 11 µmol) were used. Column chromatography (*n*-hexane/MTBE 9:1; R_f = 0.29) afforded the desired pyridothiazinethione **6b** (38 mg, 50%) as a colorless solid, mp 220–223 °C (from DCM/*n*-hexane); IR (ATR): $\tilde{\nu}$ 3024, 2963, 2902, 2879, 2869, 1641, 1597,3 1487, 1441, 1422, 1351, 1332, 1313, 1286, 1261, 1155, 1078, 1027, 987, 929, 791, 721, 697 cm^{-1}; ^1H NMR (499.9 MHz, $CDCl_3$): δ 1.75–1.76 (3 H, m, CH_3), 2.21–2.25 (1 H, m, NCHCH_2), 2.82–2.88 (1 H, m, NCHCH_2), 3.75–3.79 (1 H, m, NCH_2), 4.80 (1 H, dd, ^3J = 11.6 Hz, ^3J = 3.4 Hz, NCH), 5.52–5.53 (1 H, m, C=CH), 6.02–6.05 (1 H, m, NCH_2), 7.04–7.06 (2 H, m, 2 CH_{Ar}), 7.08–7.10 (2 H, m, 2 CH_{Ar}), 7.13–7.20 (6 H, m, 6 CH_{Ar}) ppm; ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 20.52 (CH_3), 30.27 (NCH*C*H_2), 53.76 (NCH_2), 64.51 (NCH), 120.35 (C=*C*H), 127.30 (CH*C*=C), 127.76, 128.48, 128.61, 129.20, 129.25 (10 CH_{Ar}), 130.32 (C_{Ar}), 132.81 (*C*=CH), 134.87 (C_{Ar}), 137.96 (CHC=*C*), 188.45 (C=S) ppm; MS (ESI): m/z 372.1 ($M+Na^+$, 100%); HRMS (ESI): Found 372.0857; Calc. for $C_{21}H_{19}NNaS_2$ $[M+Na]^+$ 372.0845.

(*RS*)-3,4-Bis(4-methoxyphenyl)-4a,5-dihydro-1*H*,8*H*-pyrido[1,2-*c*][1,3]thiazine-1-thione (6c): Following **GP D**, dialkene **5c** (100 mg, 0.24 mmol) and Ru-catalyst **A** (11 mg; 12 µmol) were used. Column chromatography (*n*-hexane/EtOAc 9:1; R_f = 0.16) afforded the desired pyridothiazinethione **6c** (70 mg, 75%) as a colorless solid, mp 71–74 °C (from DCM/*n*-hexane); IR (ATR): $\tilde{\nu}$ 2954, 2928, 2904, 2835, 1604, 1506, 1482, 1429, 1353, 1291, 1246, 1222, 1175, 1137, 1029, 996, 830, 657 cm^{-1}; ^1H NMR (499.9 MHz, $CDCl_3$): δ 2.27–2.31 (1 H, m, NCHCH_2), 2.87–2.94 (1 H, m, NCHCH_2), 3.74, 3.75 (6 H, 2 s, 2 OCH_3), 3.85 (1 H, ddd, ^2J = 17.6 Hz, ^3J = 4.0 Hz, ^4J = 1.8 Hz, NCH_2), 4.82 (dd, ^3J = 11.6 Hz, ^3J = 3.3 Hz, NCH), 5.77–5.85 (2 H, m, C*H*=C*H*), 6.14–6.18 (1 H, m, NCH_2), 6.69–6.74 [4 H, m, 4 *o*-CH_{Ar}(OCH_3)], 6.97–6.98 [2 H, m, 2 *o*-CH_{Ar}(CCH)], 7.02–7.03 [2 H, m, 2 *o*-CH_{Ar}(CS)] ppm; ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 30.54 (NCH*C*H_2), 50.58 (NCH_2), 55.31, 55.32 (2 OCH_3), 64.69 (NCH), 113.95, 114.07 [4 *o*-*C*H_{Ar}(OCH_3)], 125.23 (*C*H=CH), 125.93 (CH*C*=C), 126.40 (*C*H=CH), 127.21, 129.59 (2 C_{Ar}), 130.29 (CHC=*C*), 130.37, 130.52 [4 *m*-*C*H_{Ar}(OCH_3)], 158.94, 159.51 ($C_{Ar}OCH_3$), 189.08 (C=S) ppm; MS (ESI): m/z 418.1 ($M+Na^+$, 100%); HRMS (ESI): Found 418.0911; Calc. for $C_{22}H_{21}NNaO_2S_2$ $[M+Na]^+$ 418.0909.

(*RS*)-3,4-Bis(4-methoxyphenyl)-7-methyl-4a,5-dihydro-1*H*,8*H*-pyrido[1,2-*c*][1,3]-thiazine-1-thione (6d): Following **GP D**, dialkene **5d** (100 mg, 0.23 mmol) and Ru-catalyst **A** (11 mg; 12 µmol) were used. Column chromatography (DCM; R_f = 0.74) afforded the desired pyridothiazinethione **6d** (76 mg, 83%) as a colorless solid, mp 78–81 °C (from DCM/*n*-hexane); IR (ATR): $\tilde{\nu}$ 2926, 2835, 1605, 1573, 1508, 1482, 1352, 1291, 1246, 1227, 1173, 1157, 1113, 1031, 984, 931, 831, 794, 734, 595 cm^{-1}; ^1H NMR (499.9 MHz, $CDCl_3$): 1.74–1.76 (3 H, m, CCH_3), 2.21–2.24 (1 H, m, NCHCH_2), 2.79–2.87 (1 H, m, NCHCH_2), 3.74, 3.75 (6 H, 2 s, 2 OCH_3), 3.74–3.77 (1 H, m, NCH_2), 4.74 (1 H, dd, ^3J = 11.6 Hz, ^3J = 3.4

Hz, NCH), 5.52–5.53 (1 H, m, C=CH), 5.99–6.03 (1 H, m, NCH_2), 6.68–6.73 [4 H, m, 4 *o*-CH_{Ar}(OCH_3)], 6.96–6.97 [2 H, m, 2 *o*-CH_{Ar}(CCH)], 7.01–7.03 [2 H, m, 2 *o*-CH_{Ar}(CS)] ppm; ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 20.54 (CCH_3), 30.26 (NCHCH_2), 53.87 (NCH_2), 55.32, 55.33 (2 OCH_3), 64.70 (NCH), 113.98, 114.08 [4 *o*-CH_{Ar}(OCH_3)], 120.48 (C=CH), 126.12 (CHC=C), 127.33, 129.39 (2 C_{Ar}), 130.39 [2 *m*-CH_{Ar}(OCH_3)], 130.44 (CHC=C), 130.54 [2 *m*-CH_{Ar}(OCH_3)], 132.86 (C=CH), 158.97, 159.55 ($C_{Ar}OCH_3$), 188.83 (C=S) ppm; MS (ESI): m/z 432.1 (M+Na$^+$, 100%); HRMS (ESI): Found 432.1068; Calc. for $C_{23}H_{23}NNaO_2S_2$ [M+Na]$^+$ 432.1068.

(*RS*)-4-Methyl-9,10-diphenyl-2,5-dihydro-7*H*,10a*H*-[1,3]thiazino[4,3-*b*][1,3]thiazepine-7-thione (6e): Following **GP D**, dialkene **5e** (100 mg, 0.24 mmol) and Ru-catalyst **A** (11 mg; 12 µmol) were used. Column chromatography (*n*-hexane/DCM 1:1; R_f = 0.53) afforded the desired azepinethiazinethione **6e** (11 mg, 13%) as a colorless solid, mp 159–160 °C (from DCM/*n*-hexane); IR (ATR): $\tilde{\nu}$ 2914, 1598, 1467, 1443, 1330, 1236, 1163, 1135, 1086, 1010, 958, 916, 831, 780, 696 cm^{-1}; ^{1}H NMR (499.9 MHz, $CDCl_3$): δ 1.84–1.86 (3 H, m, CH_3), 2.91 (1 H, dd, ^2J = 14.4 Hz, ^3J = 8.5 Hz, SCH_2), 3.65–3.69 (1 H, m, NCH_2), 3.83 (1 H, dd, ^2J = 14.3 Hz, ^3J = 7.3 Hz, SCH_2), 5.79–5.82 (1 H, m, C=CH), 5.93 (1 H, s, NCH), 6.12–6.15 (1 H, m, NCH_2), 7.15–7.24 (10 H, m, 10 CH_{Ar}) ppm; ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 23.05 (CH_3), 26.95 (SCH_2), 57.76 (NCH_2), 68.38 (NCH), 121.53 (C=CH), 124.49 (CHC=C), 127.93, 128.65, 128.80, 129.22, 130.15 (10 CH_{Ar}), 134.40 (C_{Ar}), 135.53 (C=CH), 137.46 (CHC=C), 138.18 (C_{Ar}), 189.83 (C=S) ppm; MS (ESI): m/z 404.1 (M+Na$^+$, 100%); HRMS (ESI): Found 404.0577; Calc. for $C_{21}H_{19}NNaS_3$ [M+Na]$^+$ 404.0575.

(*RS*)-9,10-Bis(4-methoxyphenyl)-4-methyl-2,5-dihydro-7*H*,10a*H*-[1,3]thiazino[4,3-*b*][1,3]oxazepine-7-thione (6f): Following **GP D**, dialkene **5f** (100 mg, 0.22 mmol) and Ru-catalyst **A** (10 mg; 11 µmol) were used. Column chromatography (*n*-hexane/EtOAc 7:3; R_f = 0.47) afforded the desired azepinethiazinethione **6f** (45 mg, 50%) as a brown oil; IR (ATR): $\tilde{\nu}$ 2935, 2835, 1603, 1506, 1468, 1413, 1327, 1292, 1244, 1175, 1155, 1093, 1028, 987, 962, 828, 681 cm^{-1}; ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 1.93–1.95 (3 H, m, CCH_3), 3.75, 3.76 (6 H, 2 s, 2 OCH_3), 3.86–3.89 (1 H, m, NCH_2), 4.36–4.40 (1 H, m, OCH_2), 4.48–4.52 (1 H, m, OCH_2), 5.60–5.62 (1 H, m, C=CH), 5.75 (1 H, s, NCH), 5.77–5.80 (1 H, m, NCH_2), 6.72–6.74 [4 H, m, 4 *o*-CH_{Ar}(OCH_3)], 7.04–7.07 [2 H, m, 2 *o*-CH_{Ar}(CCH)], 7.15–7.18 [2 H, m, 2 *o*-CH_{Ar}(CS)] ppm; ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 23.23 (CCH_3), 55.31, 55.33 (2 OCH_3), 56.73 (NCH_2), 66.17 (OCH_2), 91.82 (NCH), 113.94, 114.04 [4 *o*-CH_{Ar}(OCH_3)], 122.51 (C=CH), 124.57 (CHC=C), 126.51, 130.14 (2 C_{Ar}), 130.27, 131.41 [4 *m*-CH_{Ar}(OCH_3)], 135.35 (CHC=C), 138.21 (C=CH), 158.96, 160.05 ($C_{Ar}OCH_3$), 190.52 (C=S) ppm; MS (ESI): m/z 448.1 (M+Na$^+$, 100%); HRMS (ESI): Found 448.1017; Calc. for $C_{23}H_{23}NNaO_3S_2$ [M+Na]$^+$ 448.1013.

X-ray crystal structures

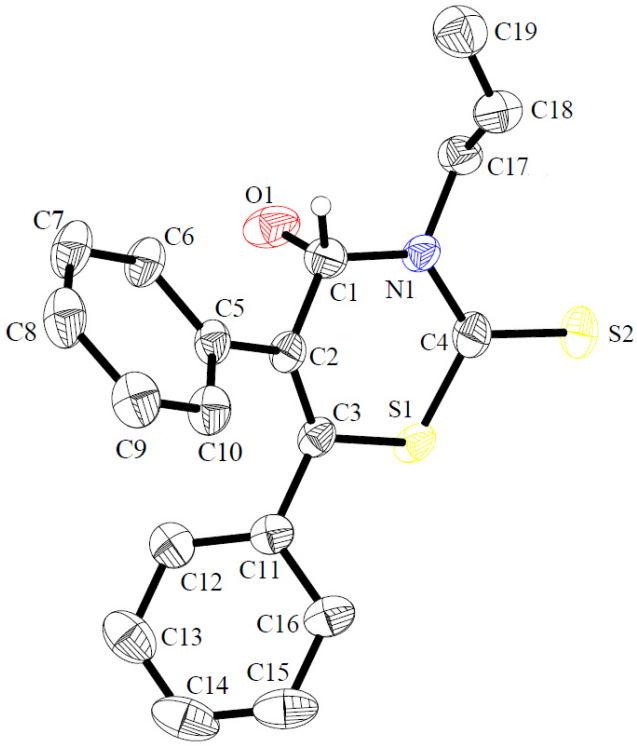


Figure S1. X-ray crystal structure of the racemic 2*H*-1,3-thiazine-2-thione **2a** (only one enantiomer is shown). The atom numbering does not follow the IUPAC nomenclature.

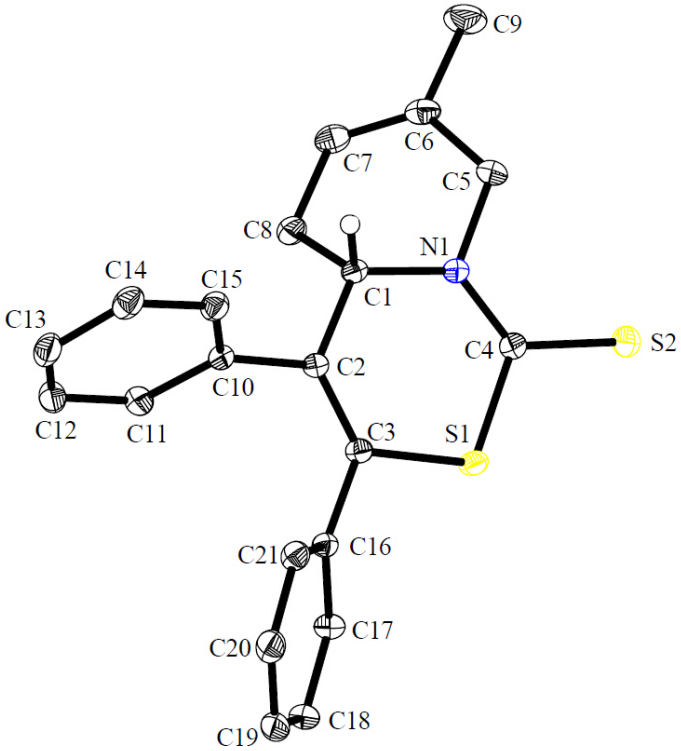
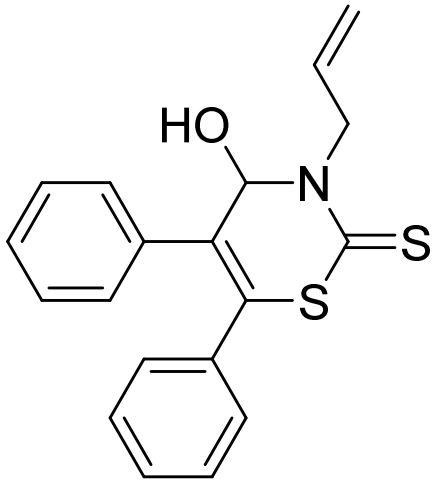
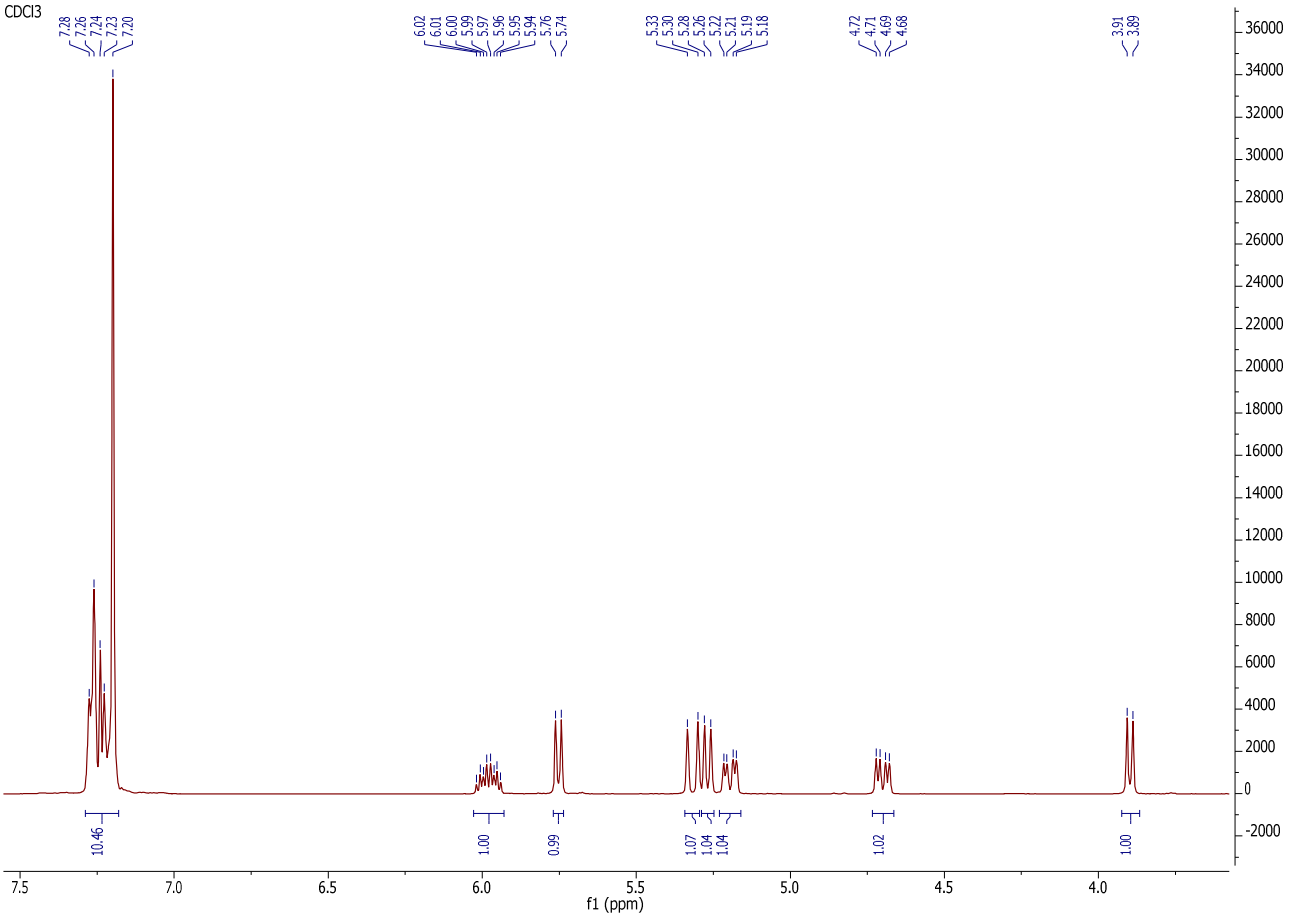


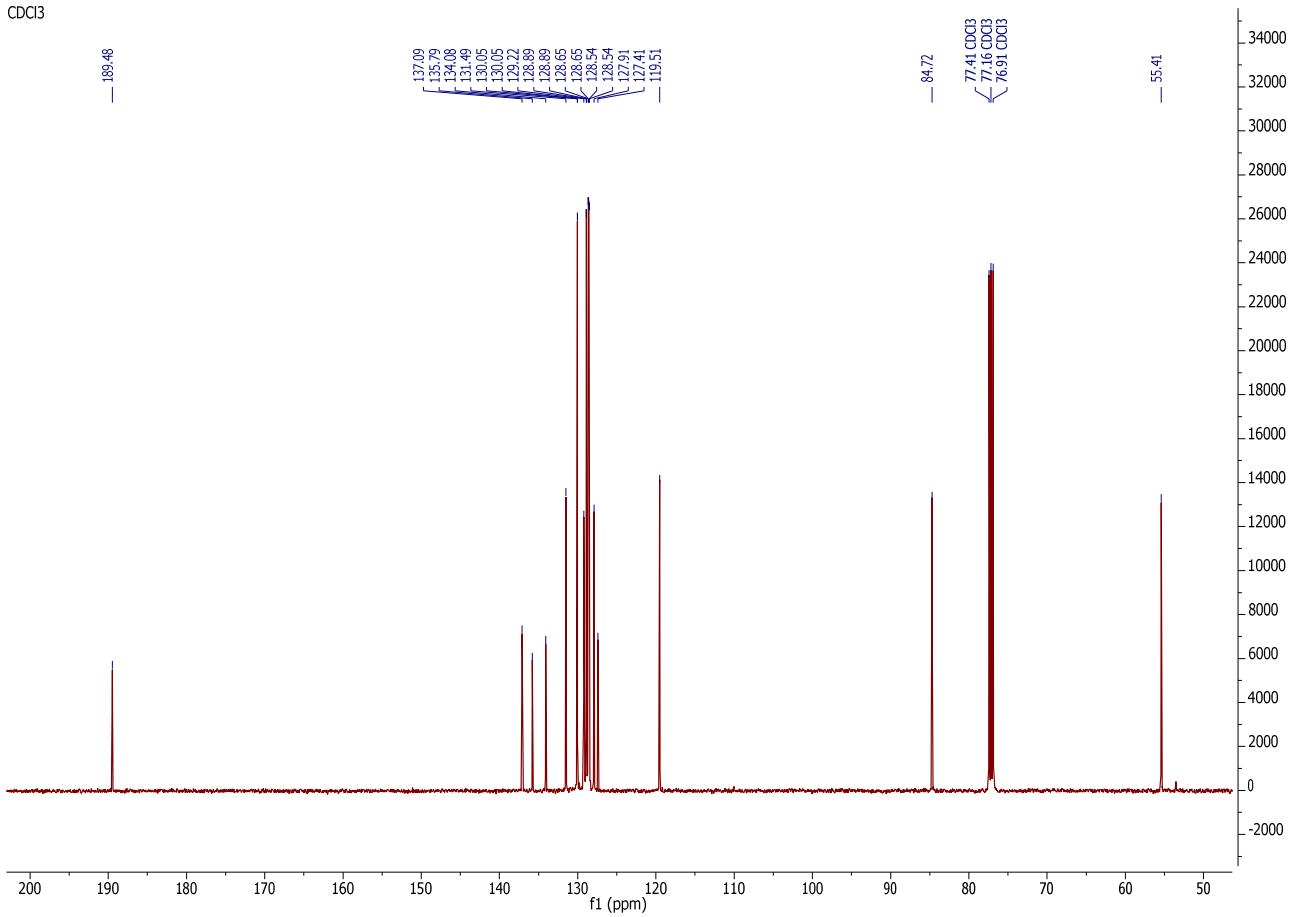
Figure S2. X-ray crystal structure of the racemic pyridothiazinethiones **6b** (only one enantiomer is shown). The atom numbering does not follow the IUPAC nomenclature.

NMR spectra



2a

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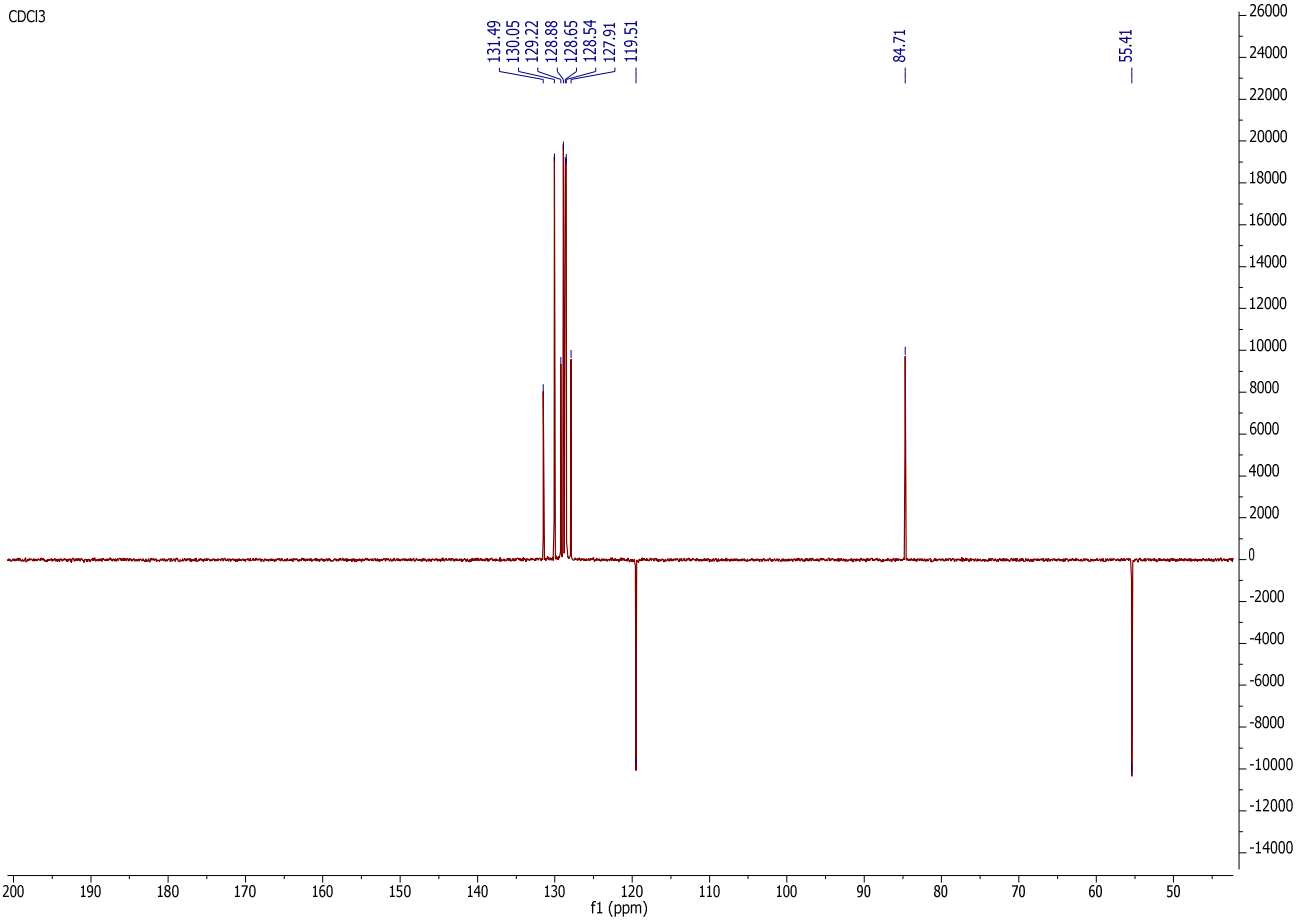
135.79
134.08
131.49
130.05
130.05
129.22
128.89
128.89
128.65
128.65
128.54
128.54
127.91
127.41
119.51
84.72
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
55.41
f1 (ppm)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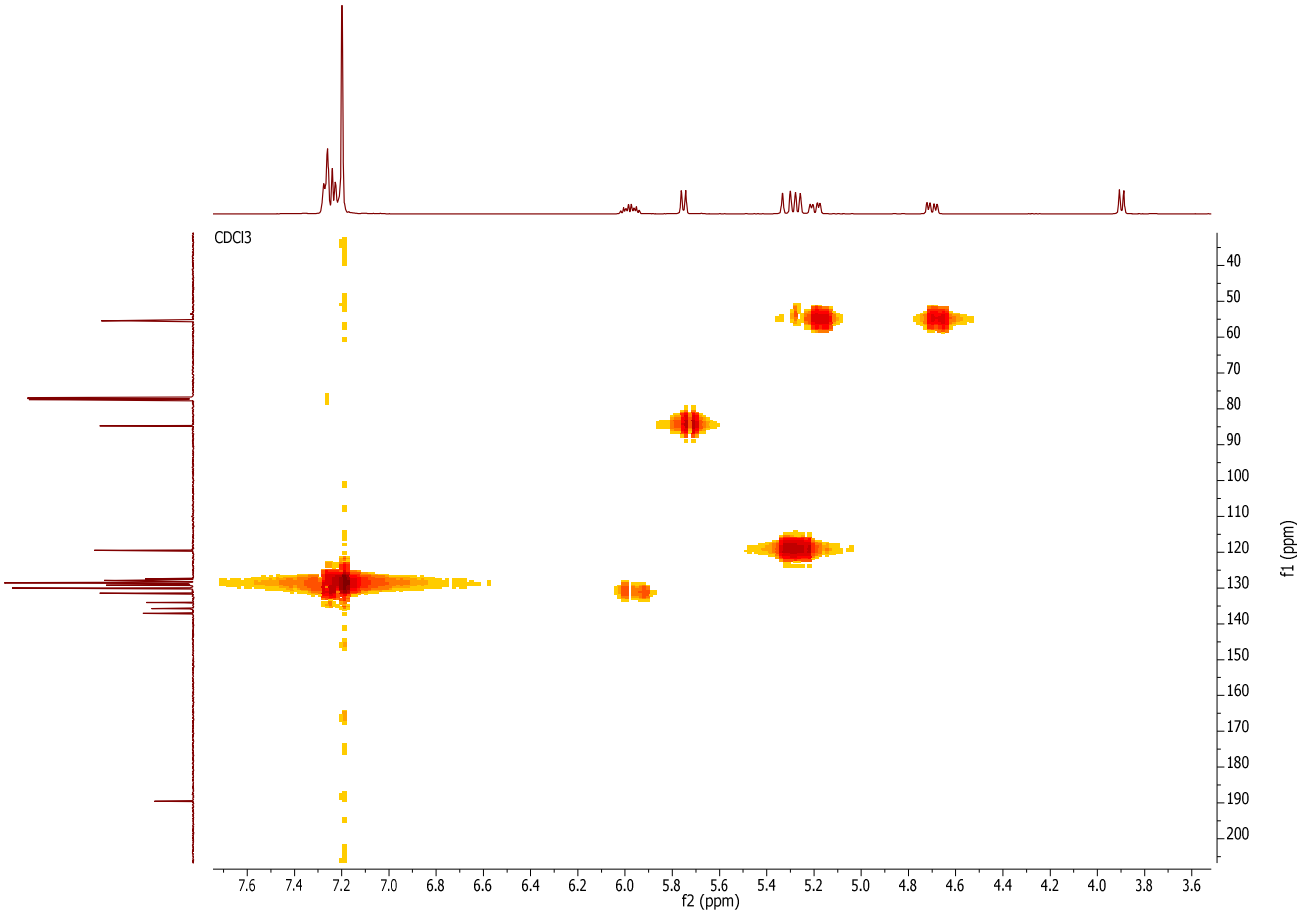
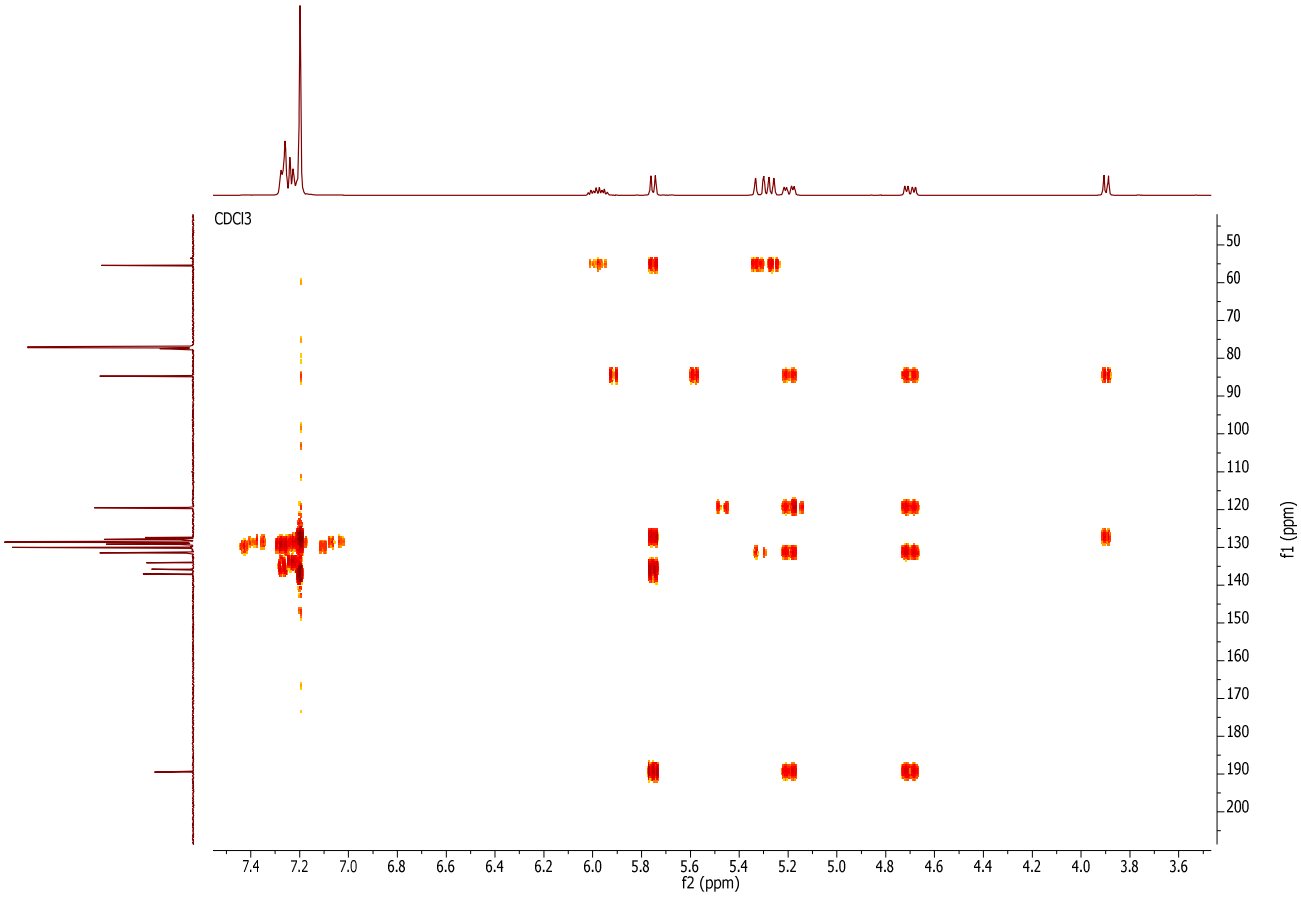
f1 (ppm)


CDCl3
f2 (ppm)
f1 (ppm)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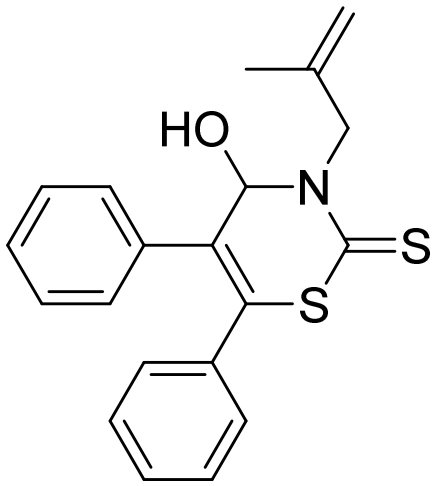
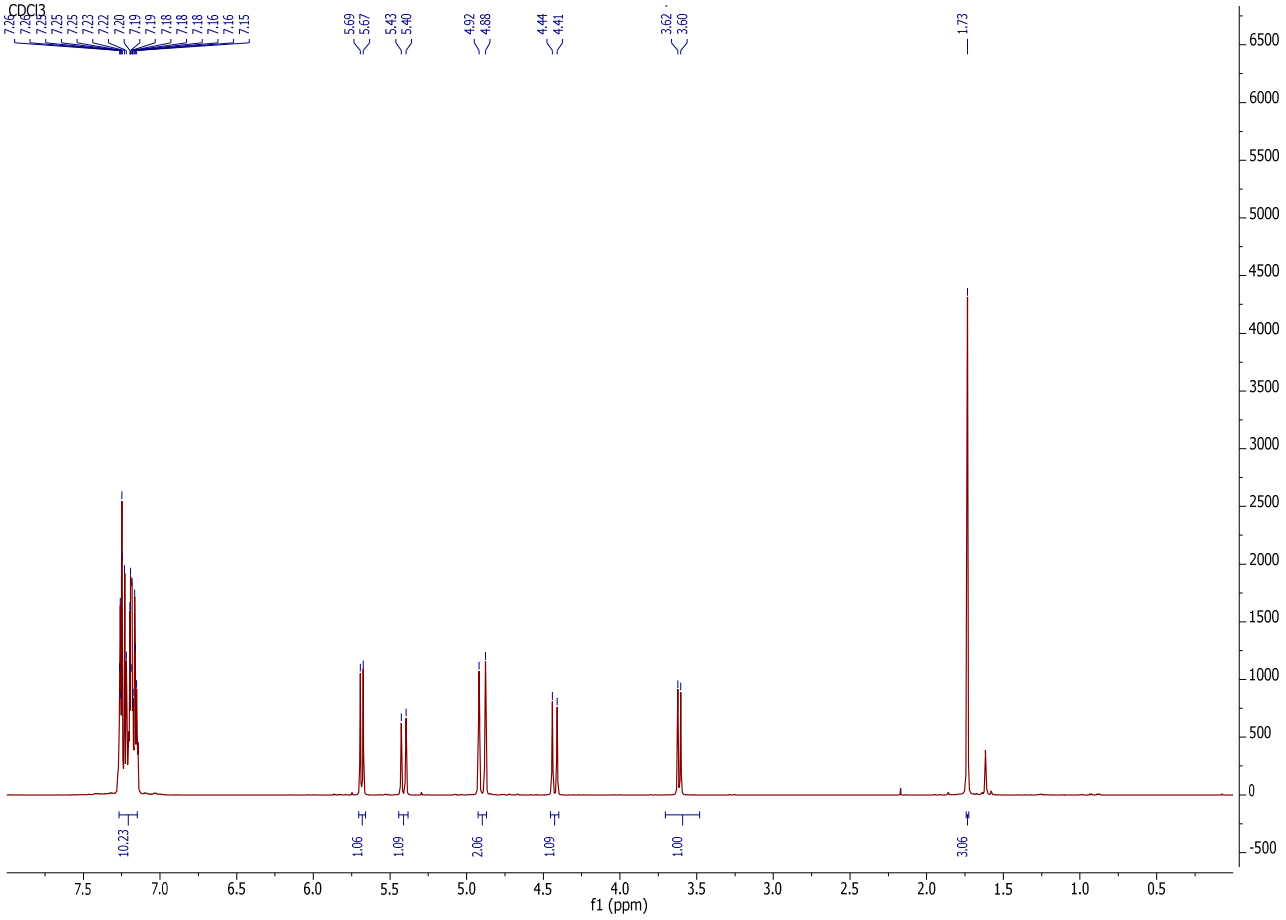
f2 (ppm)
f1 (ppm)


HO
N
S
S

2b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7.19
7.18
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7.16
7.15
5.69
5.67
5.43
5.40
4.92
4.88
4.44
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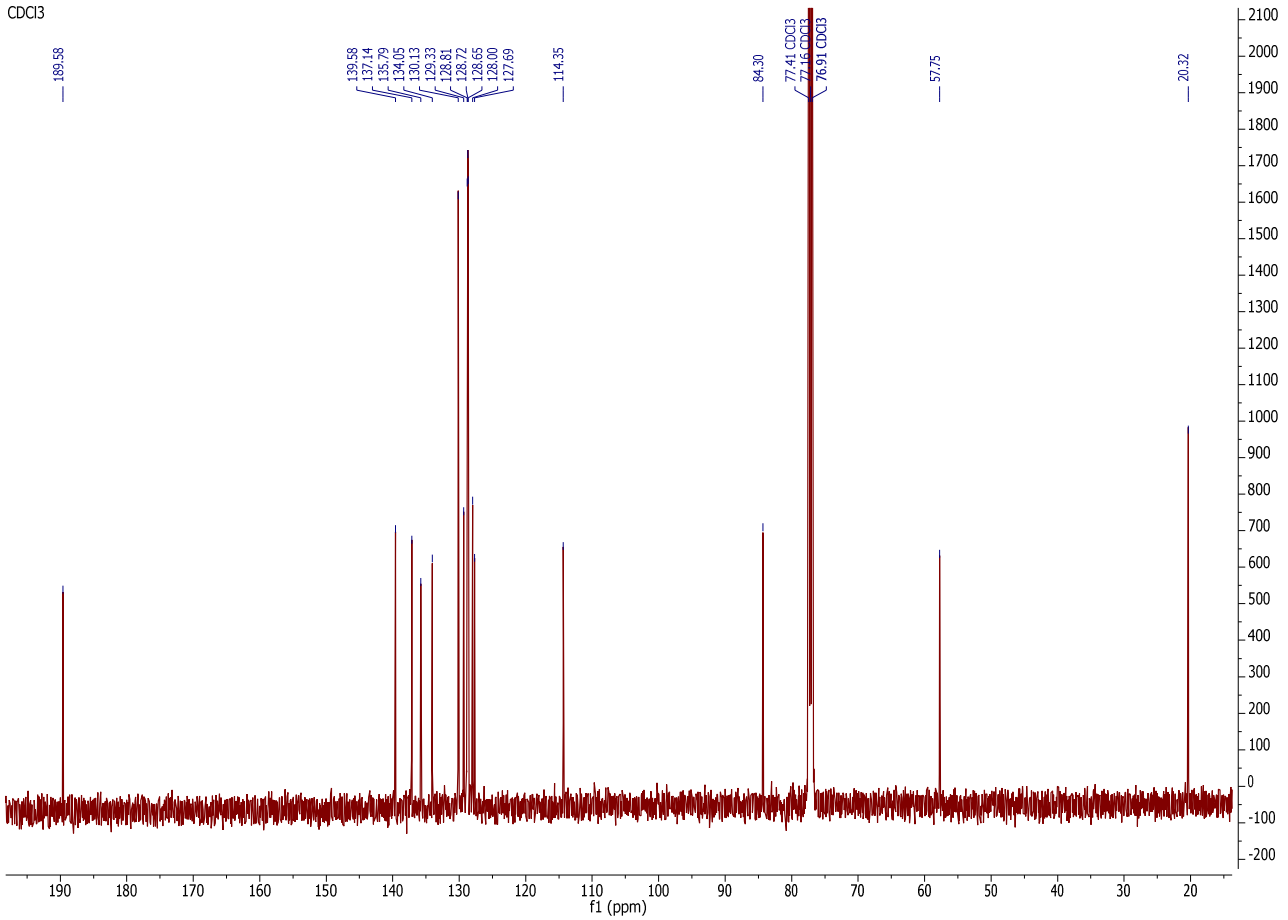
2.06
1.09
1.00
3.06
f1 (ppm)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128.72
128.65
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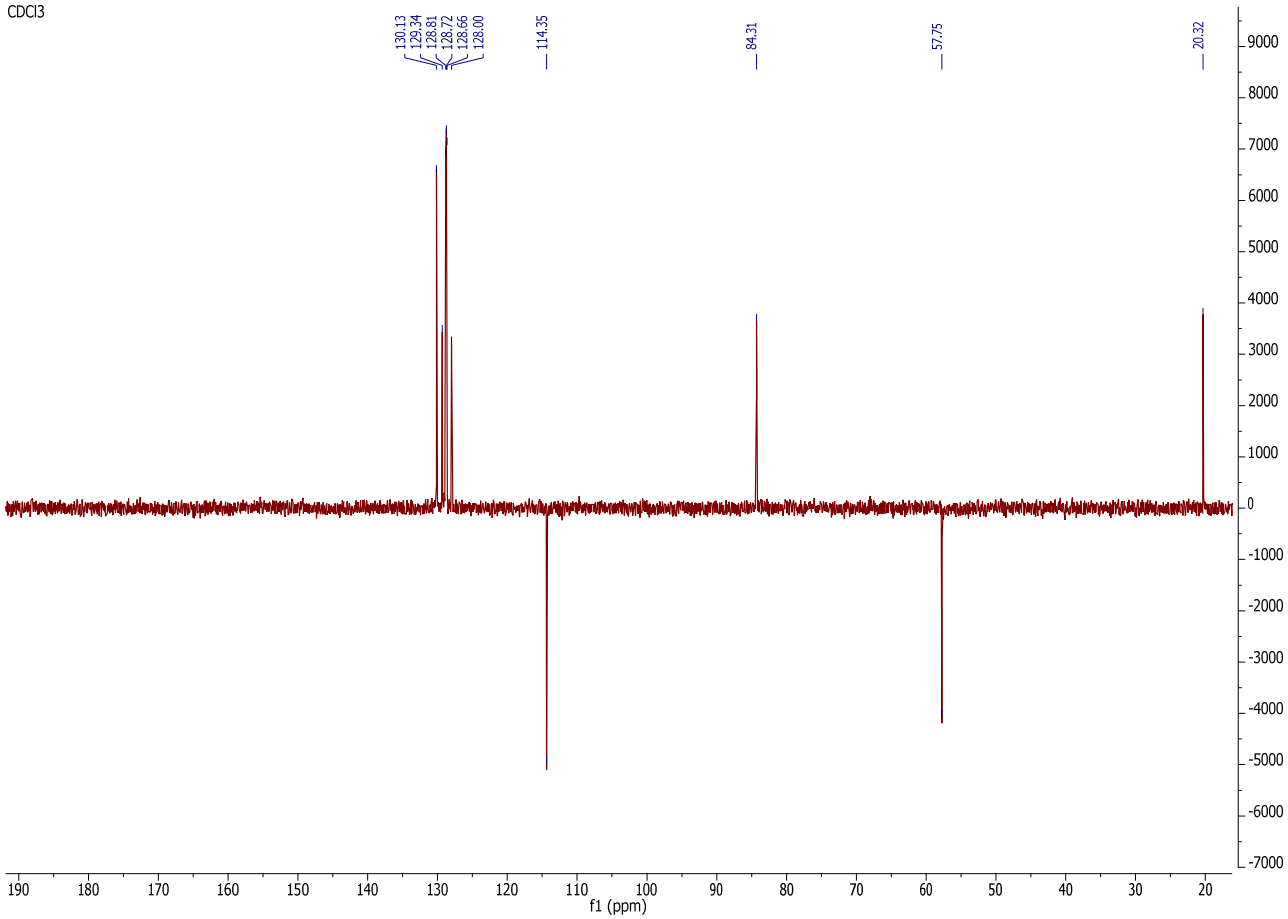
76.91 CDCl3
57.75
20.32
f1 (ppm)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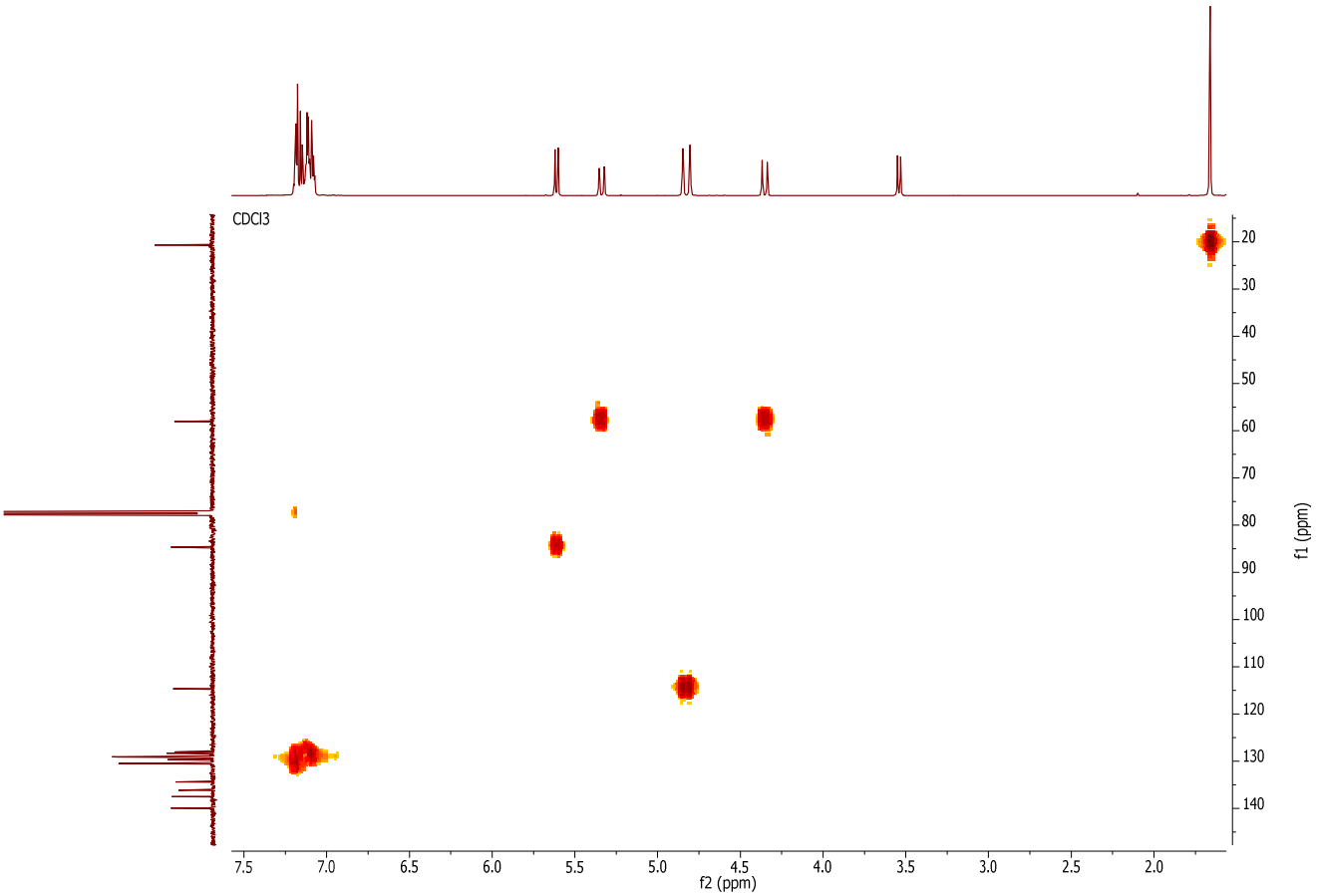
84.31
57.75
20.32
f1 (ppm)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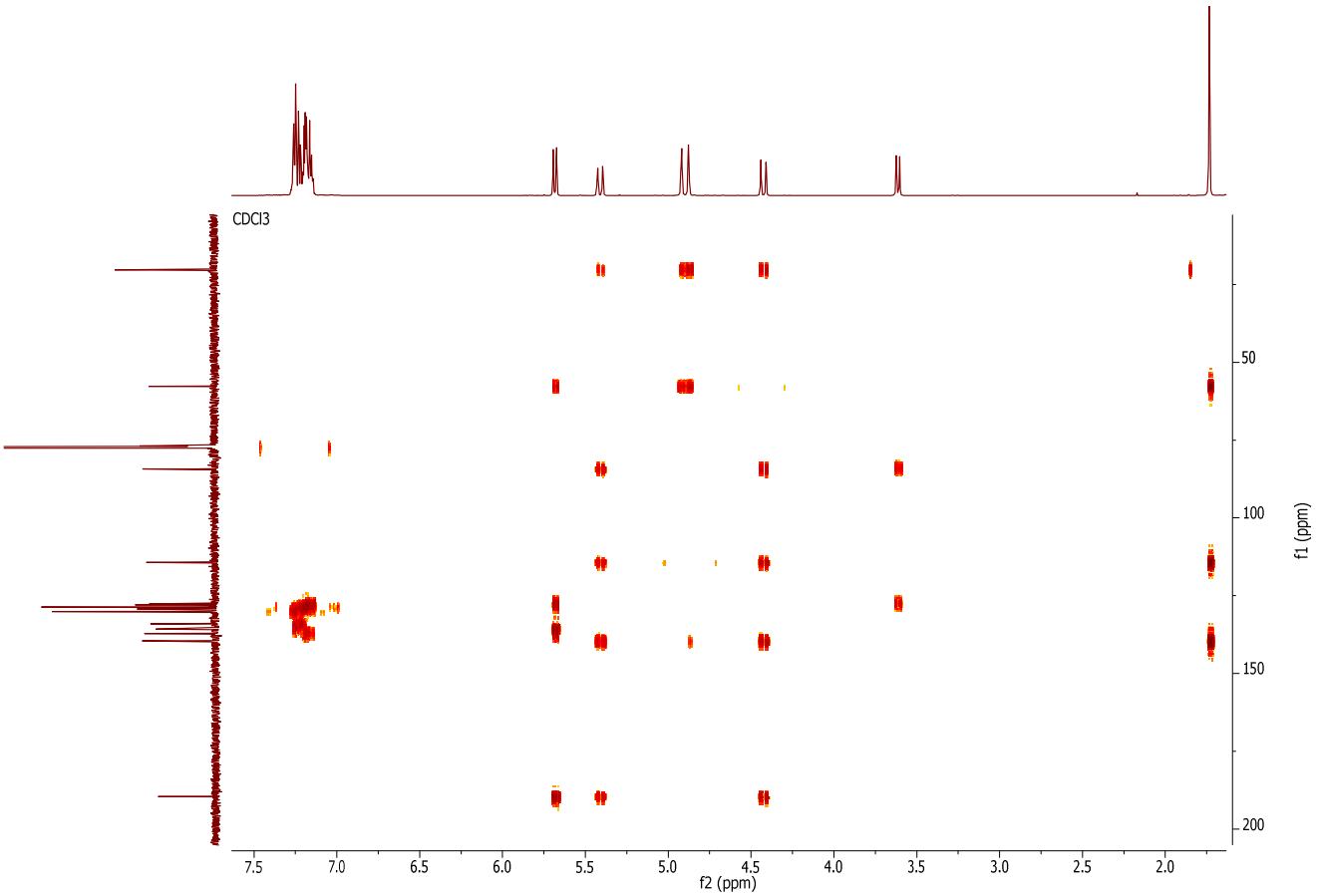
f2 (ppm)
f1 (ppm)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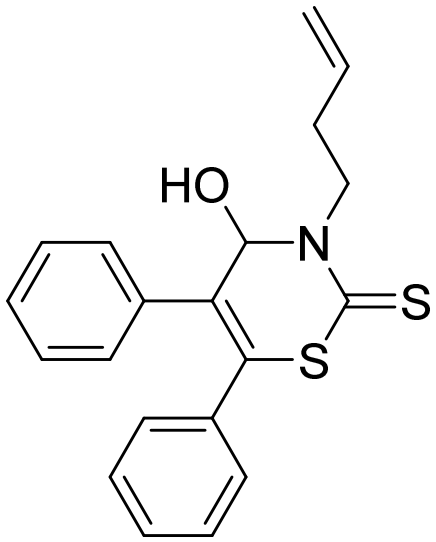
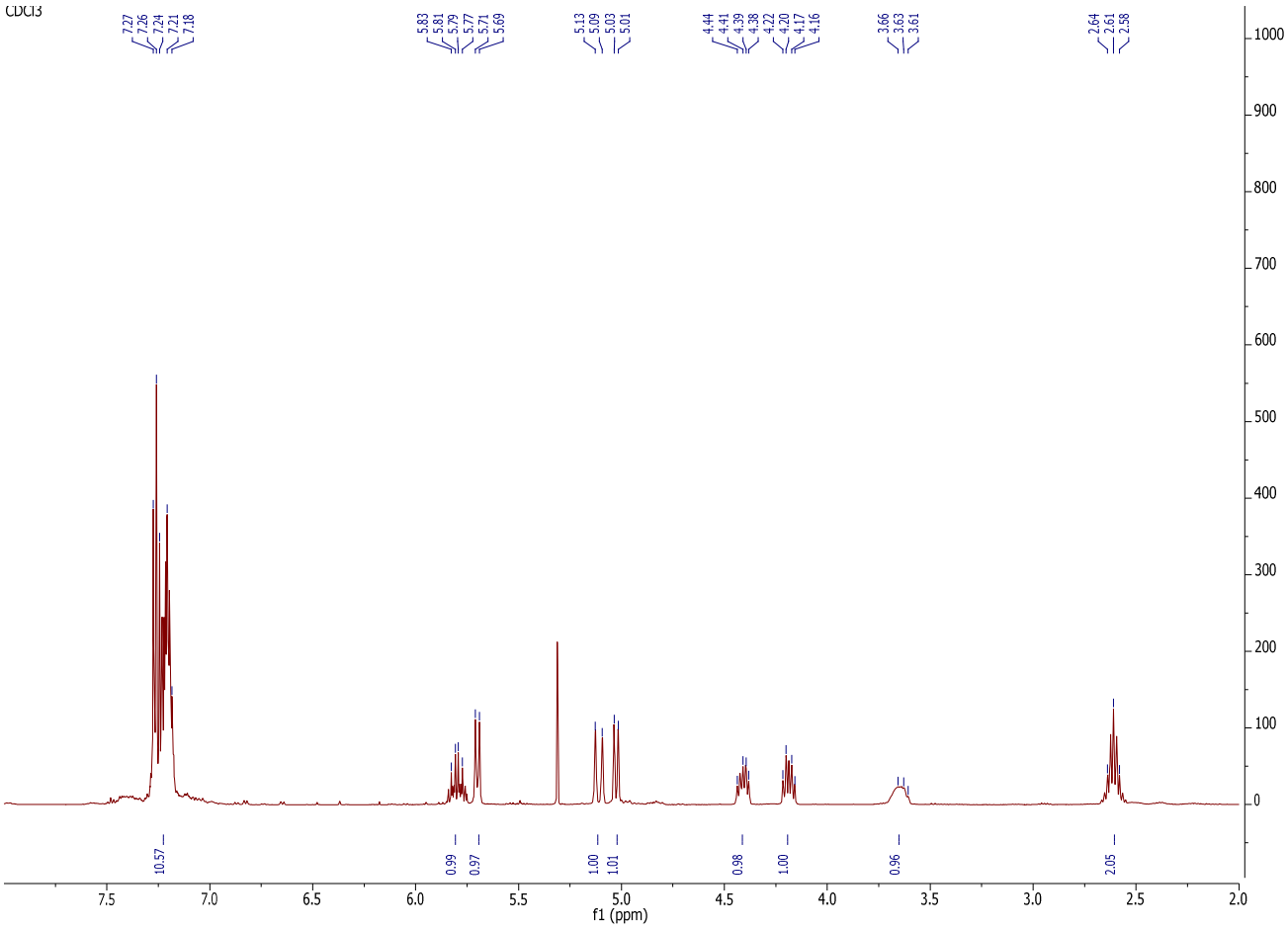
f2 (ppm)
f1 (ppm)


HO
N
S
S

2c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7.18
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5.81
5.79
5.77
5.71
5.69
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5.09
5.03
5.01
4.44
4.41
4.39
4.38
4.22
4.20
4.17
4.16
3.66
3.63
3.61
2.64
2.61
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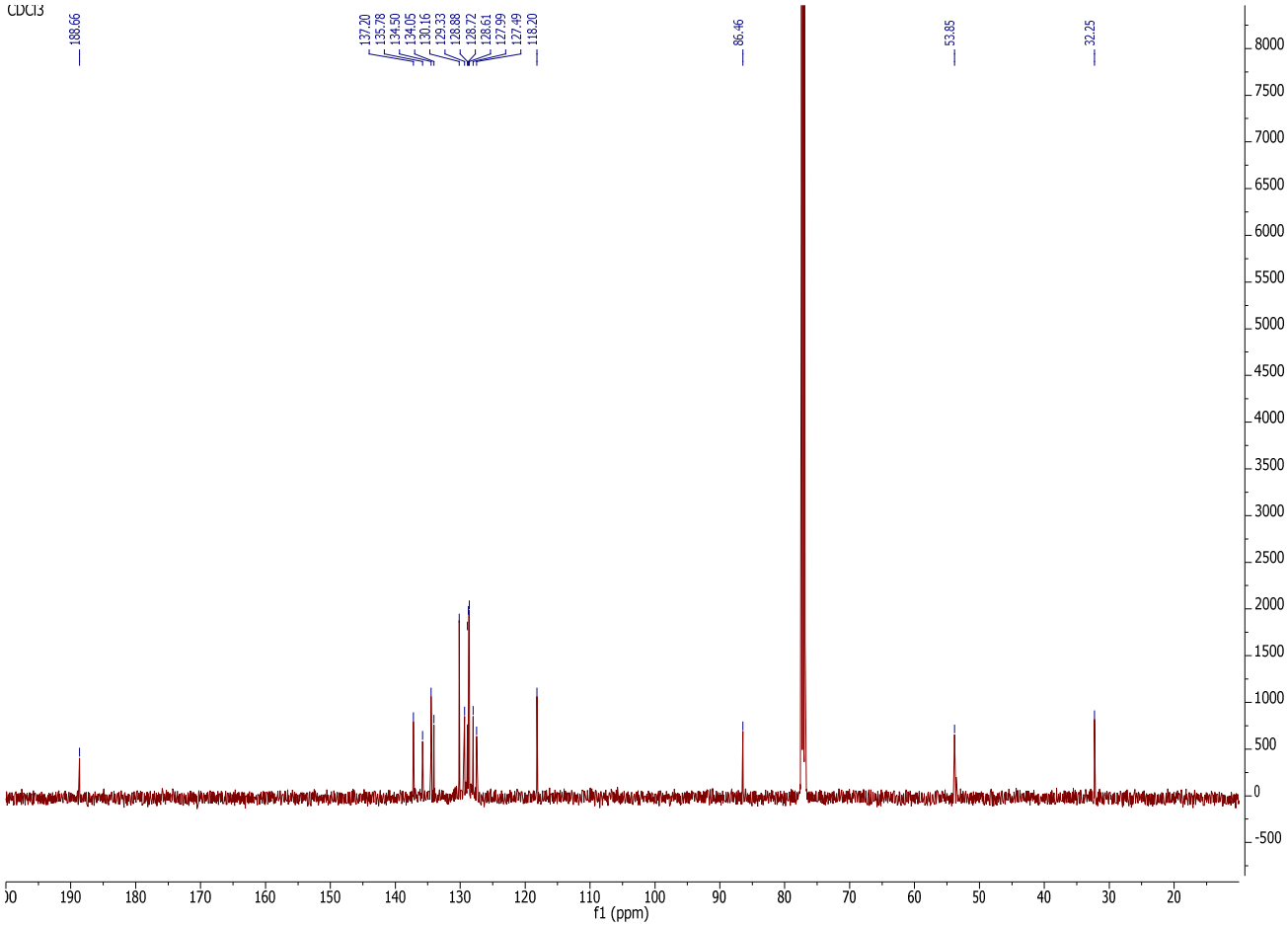
1.00
1.01
0.98
1.00
0.96
2.05
f1 (ppm)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134.05
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128.72
128.61
127.99
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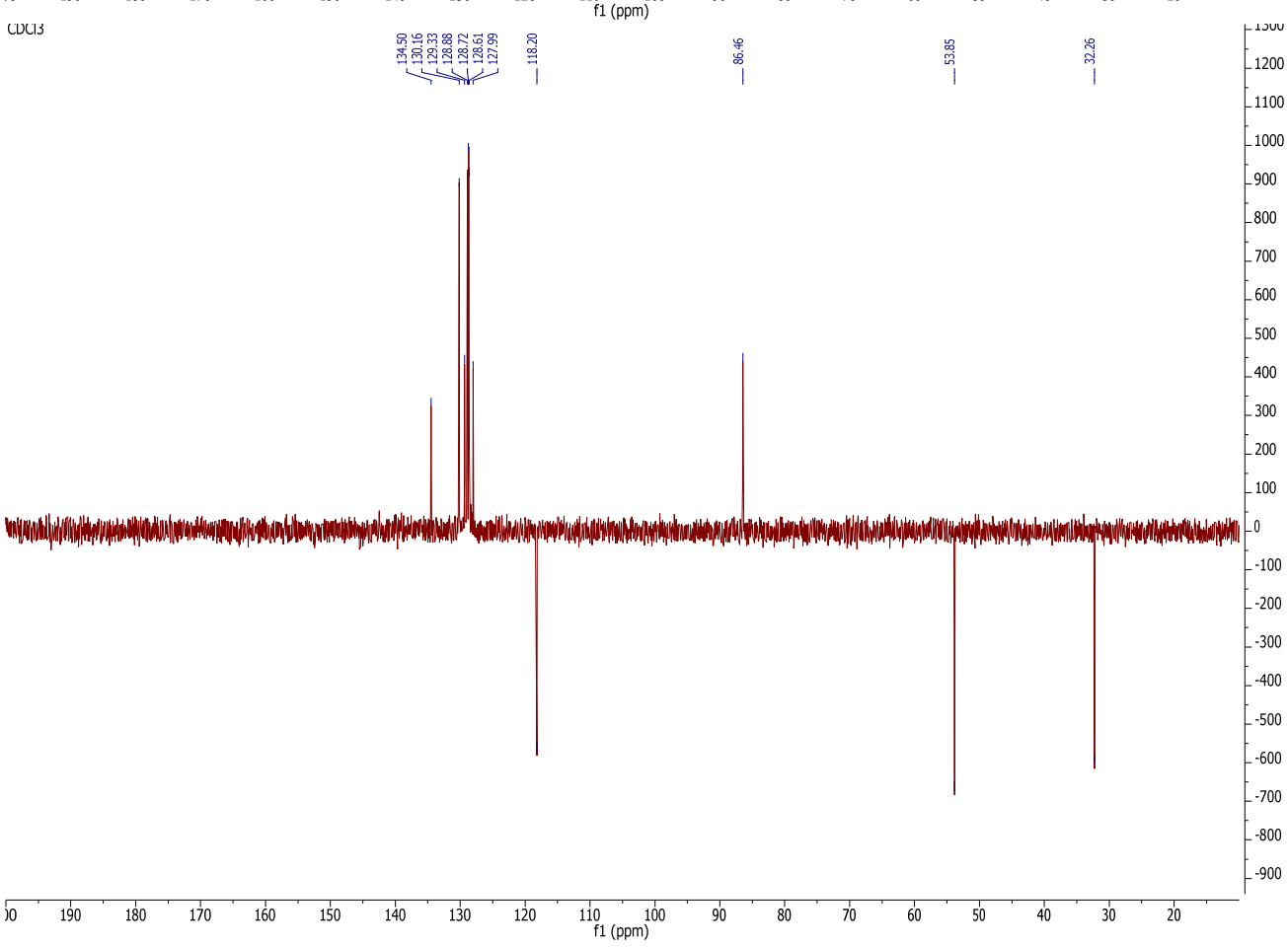
118.20
86.46
53.85
32.25
f1 (ppm)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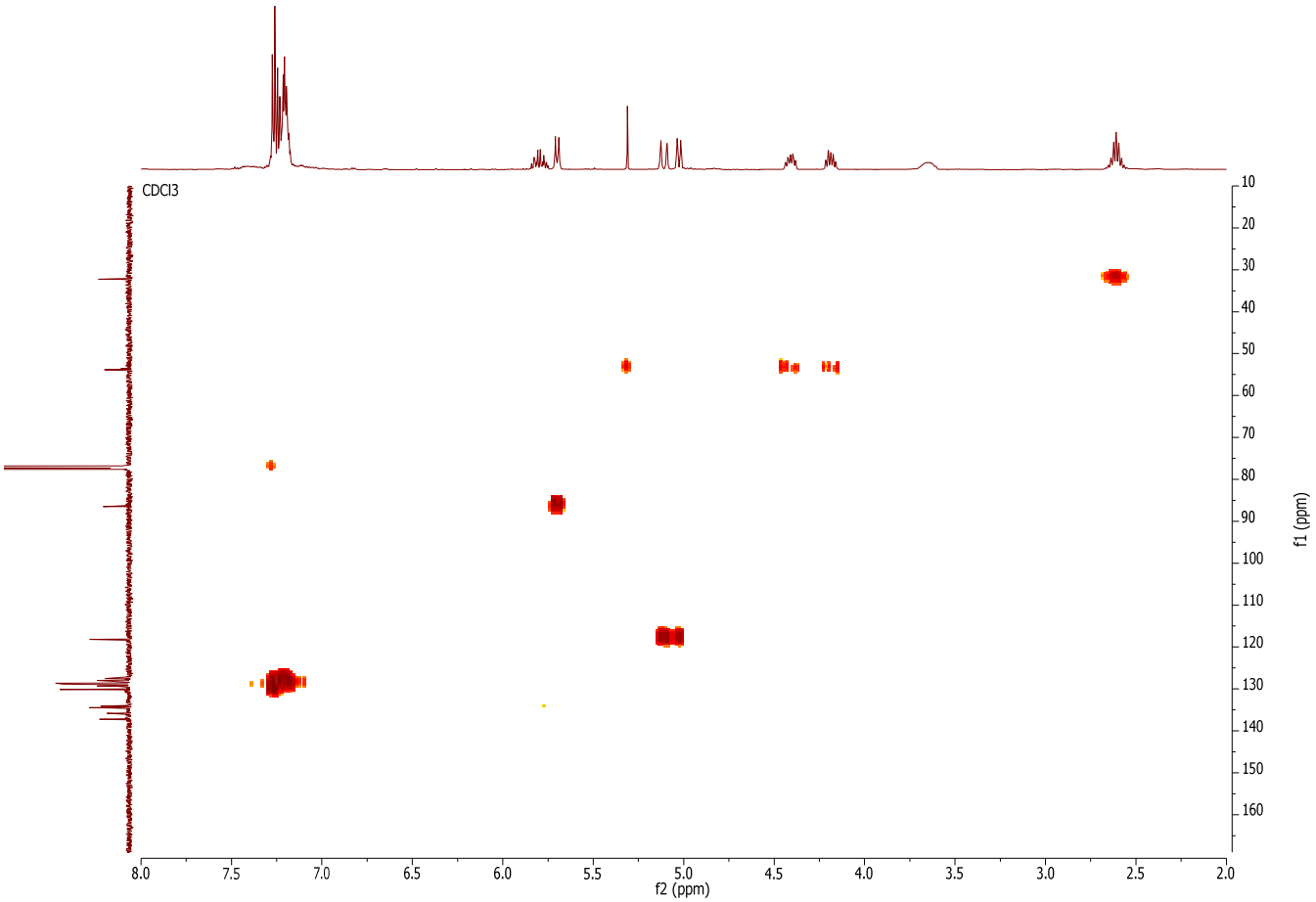
128.61
127.99
118.20
86.46
53.85
32.26
f1 (ppm)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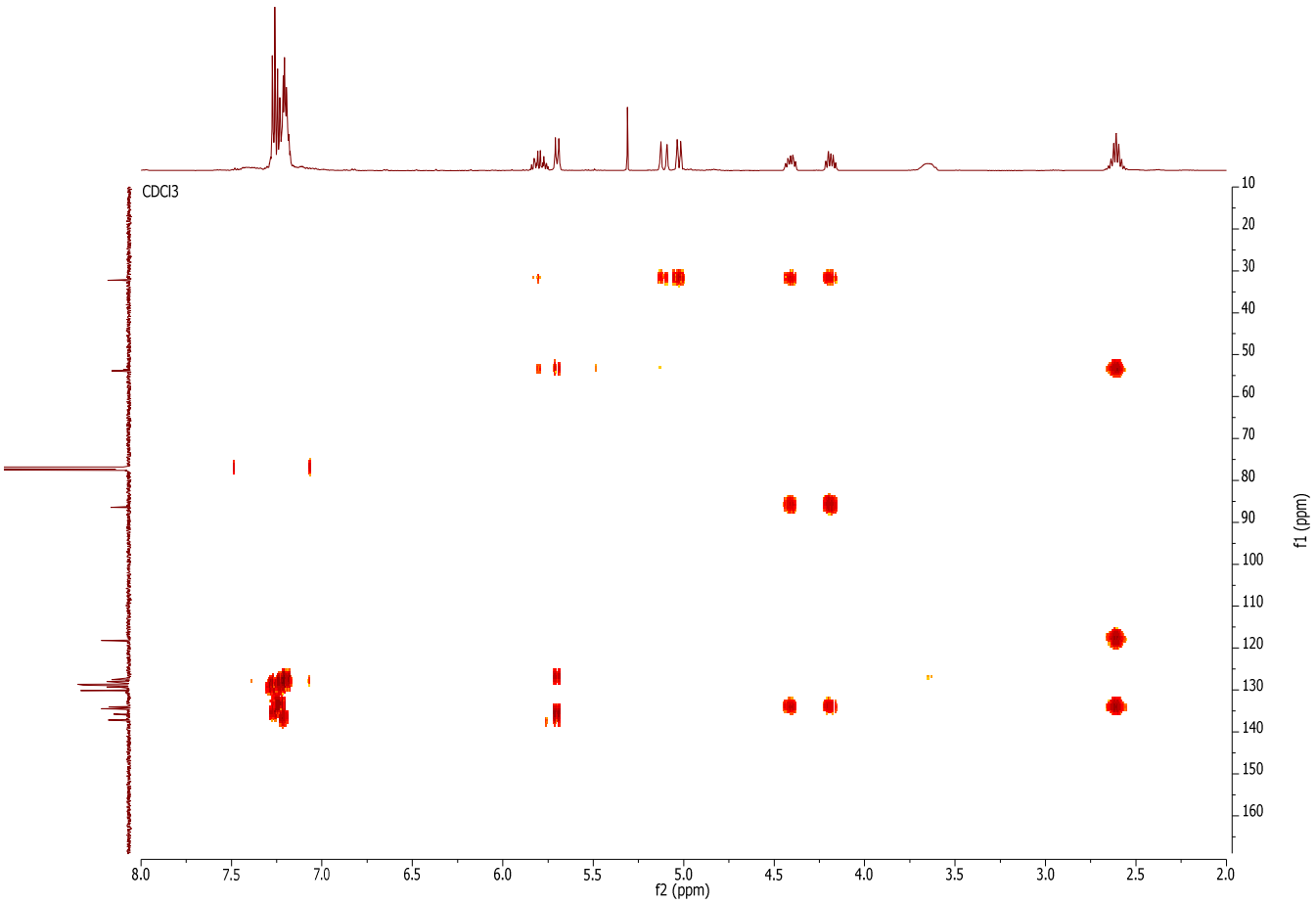
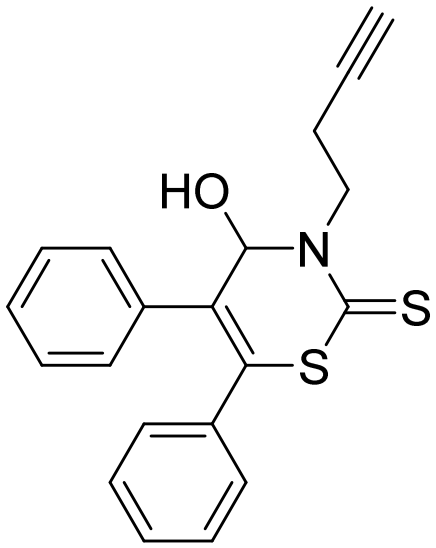
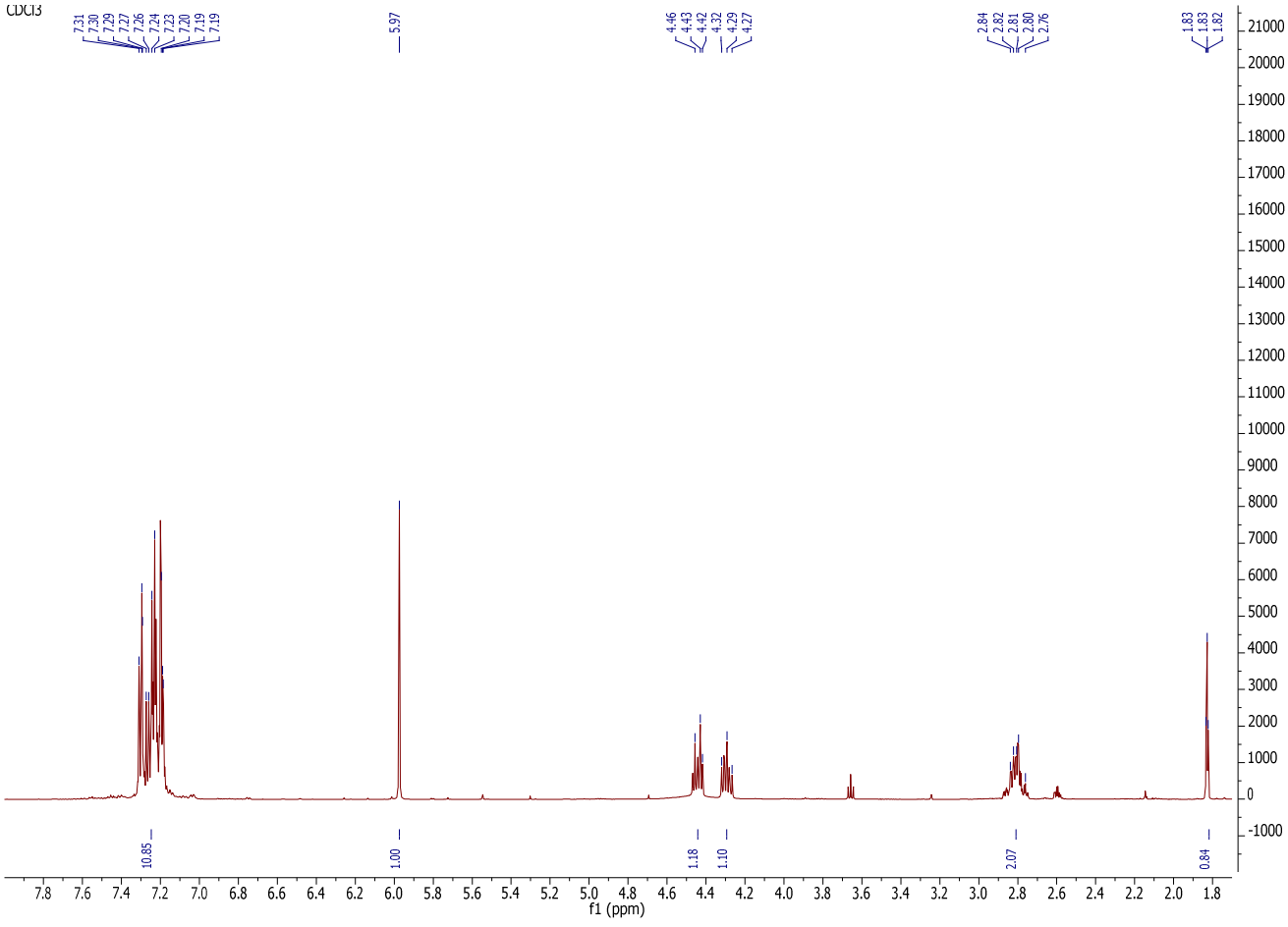
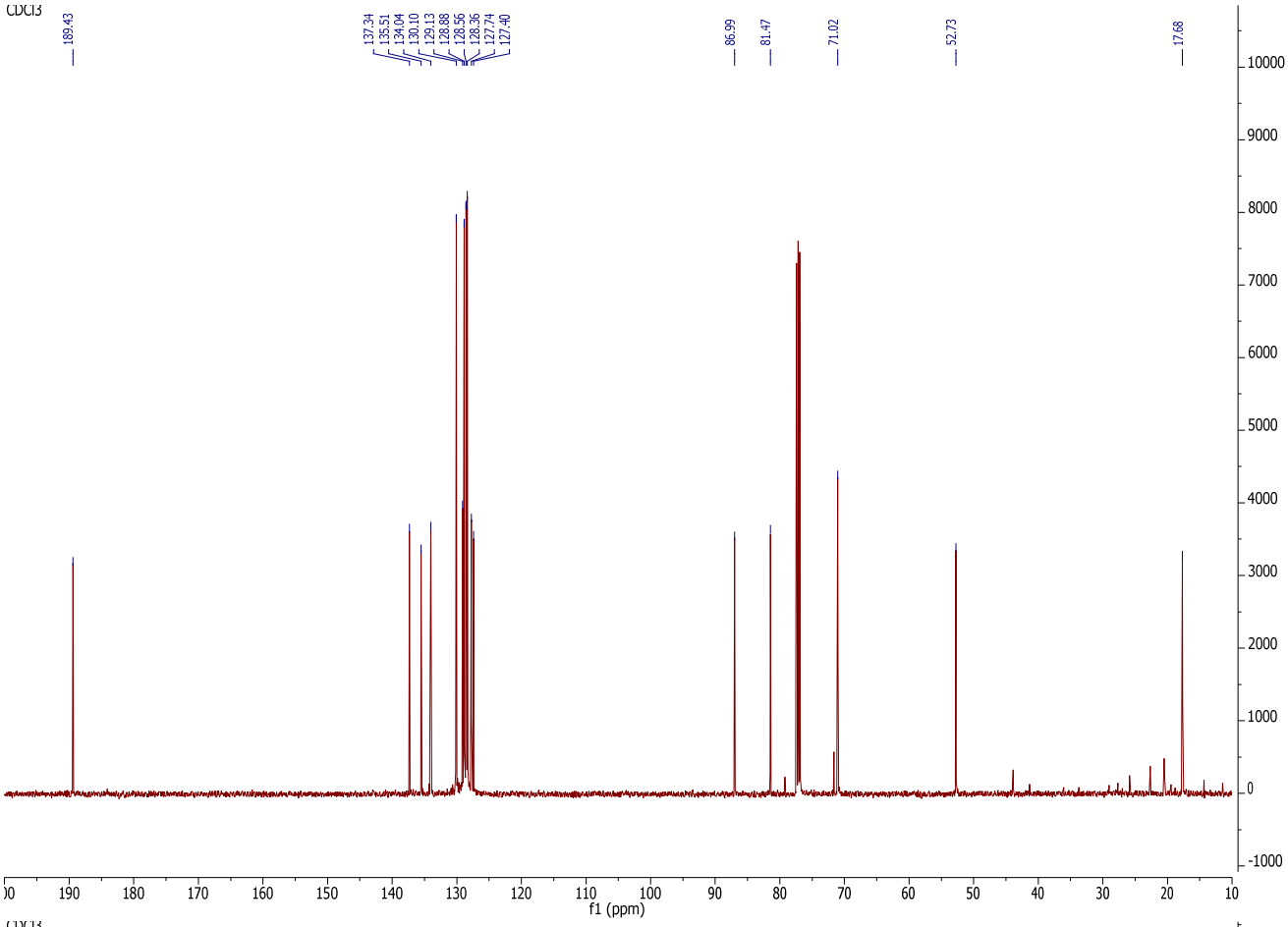
f2 (ppm)
f1 (ppm)

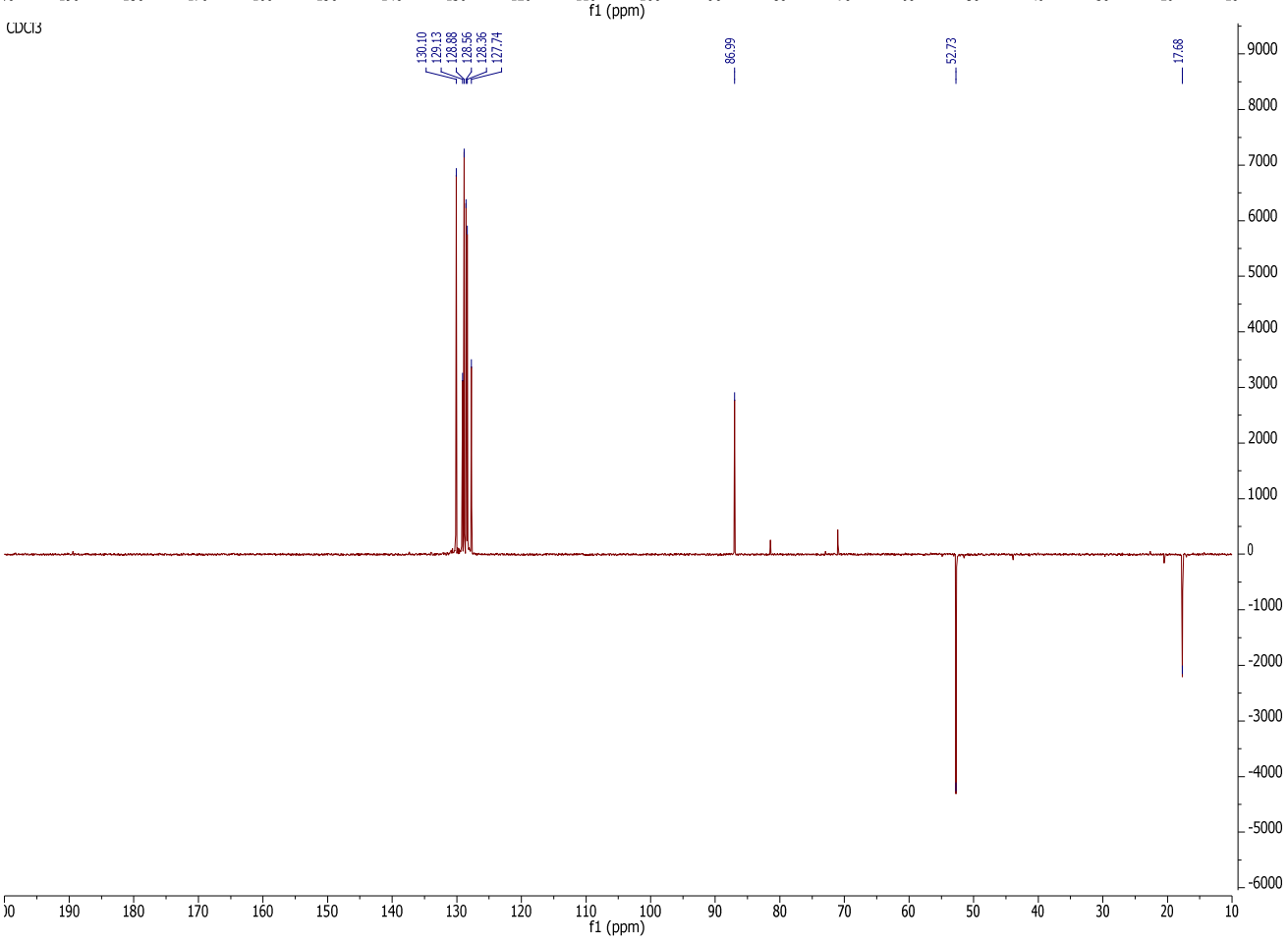

CDCl3
f2 (ppm)
f1 (ppm)

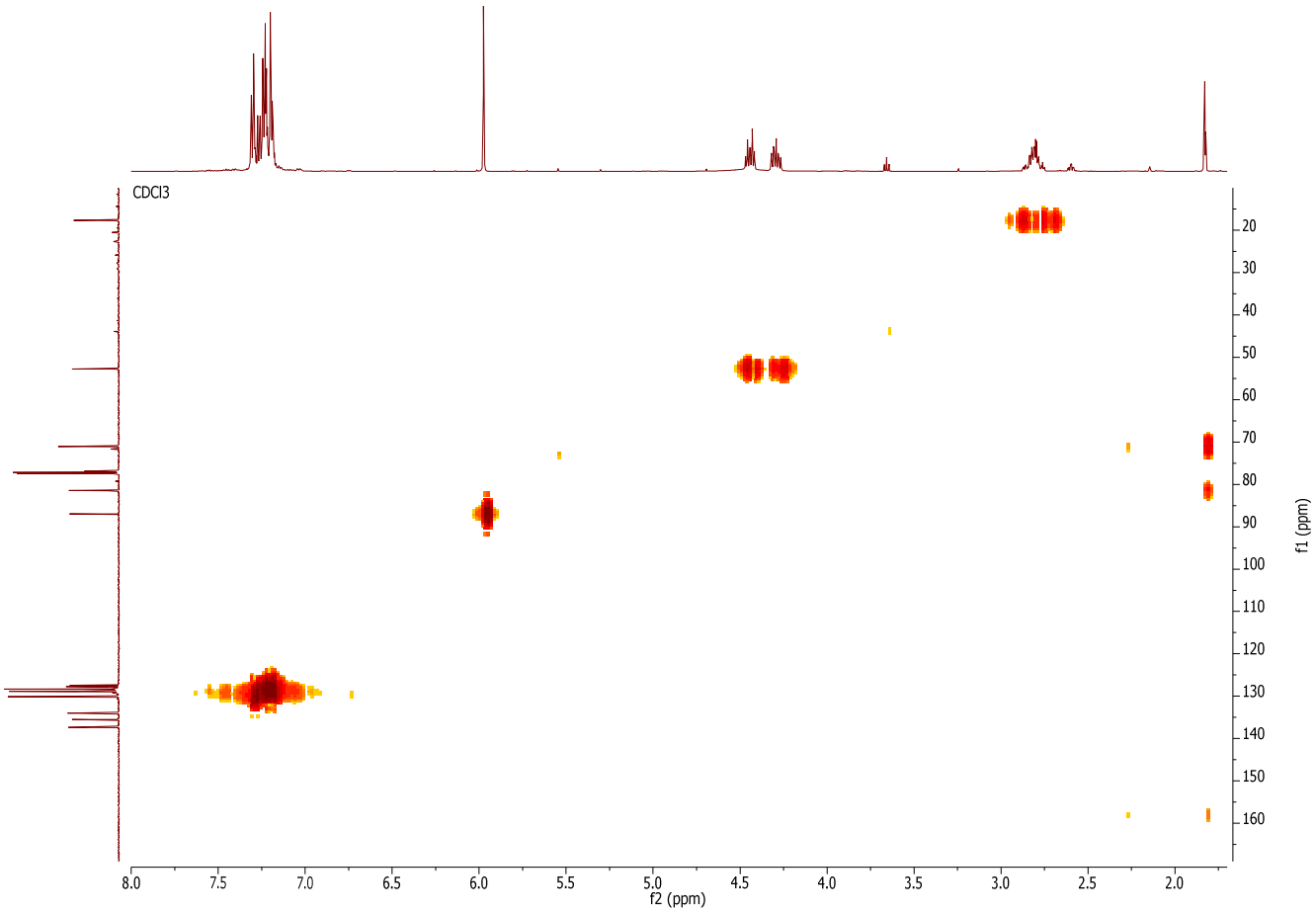

HO
N
S
S

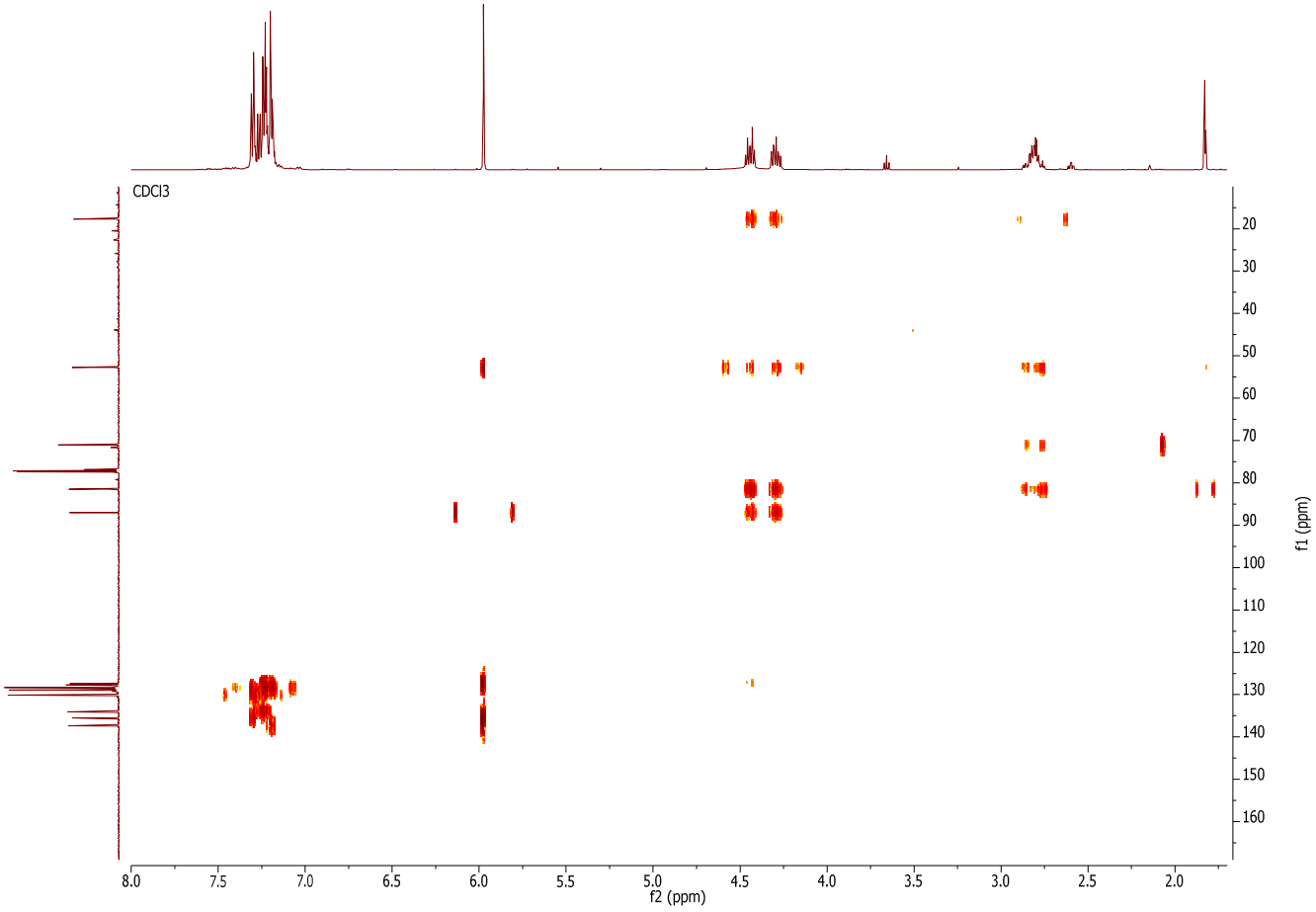
2d

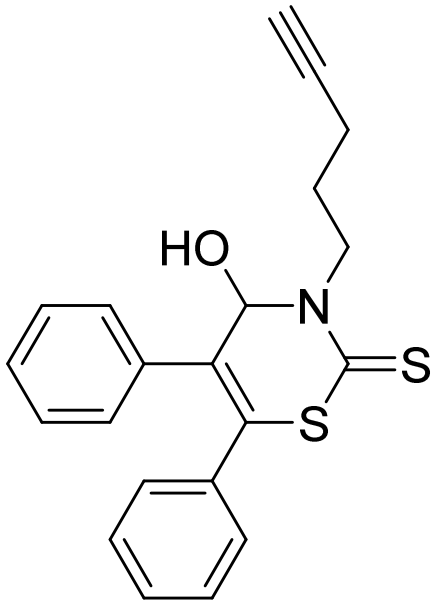

CDCl3
7.31
7.30
7.29
7.27
7.26
7.24
7.23
7.20
7.19
7.19
5.97
4.46
4.43
4.42
4.32
4.29
4.27
2.84
2.82
2.81
2.80
2.76
1.83
1.83
1.82
10.85
1.00
1.18
1.10
2.07
0.84
f1 (ppm)


CDCl3
189.43
137.34
135.51
134.04
130.10
129.13
128.88
128.56
128.36
127.74
127.40
86.99
81.47
71.02
52.73
17.68
f1 (ppm)

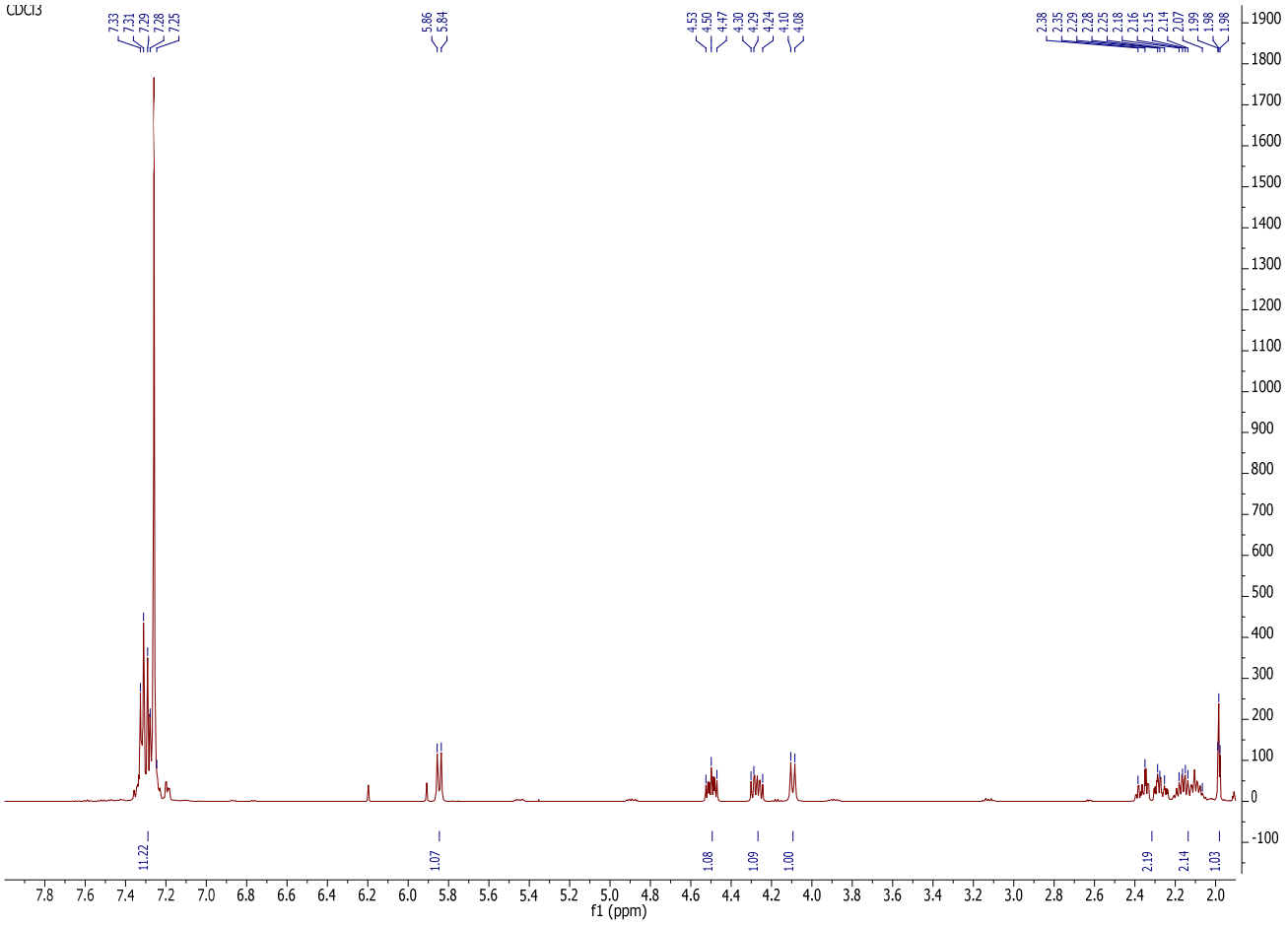

CDCl3
130.10
129.13
128.88
128.56
128.36
127.74
86.99
52.73
17.68
f1 (ppm)

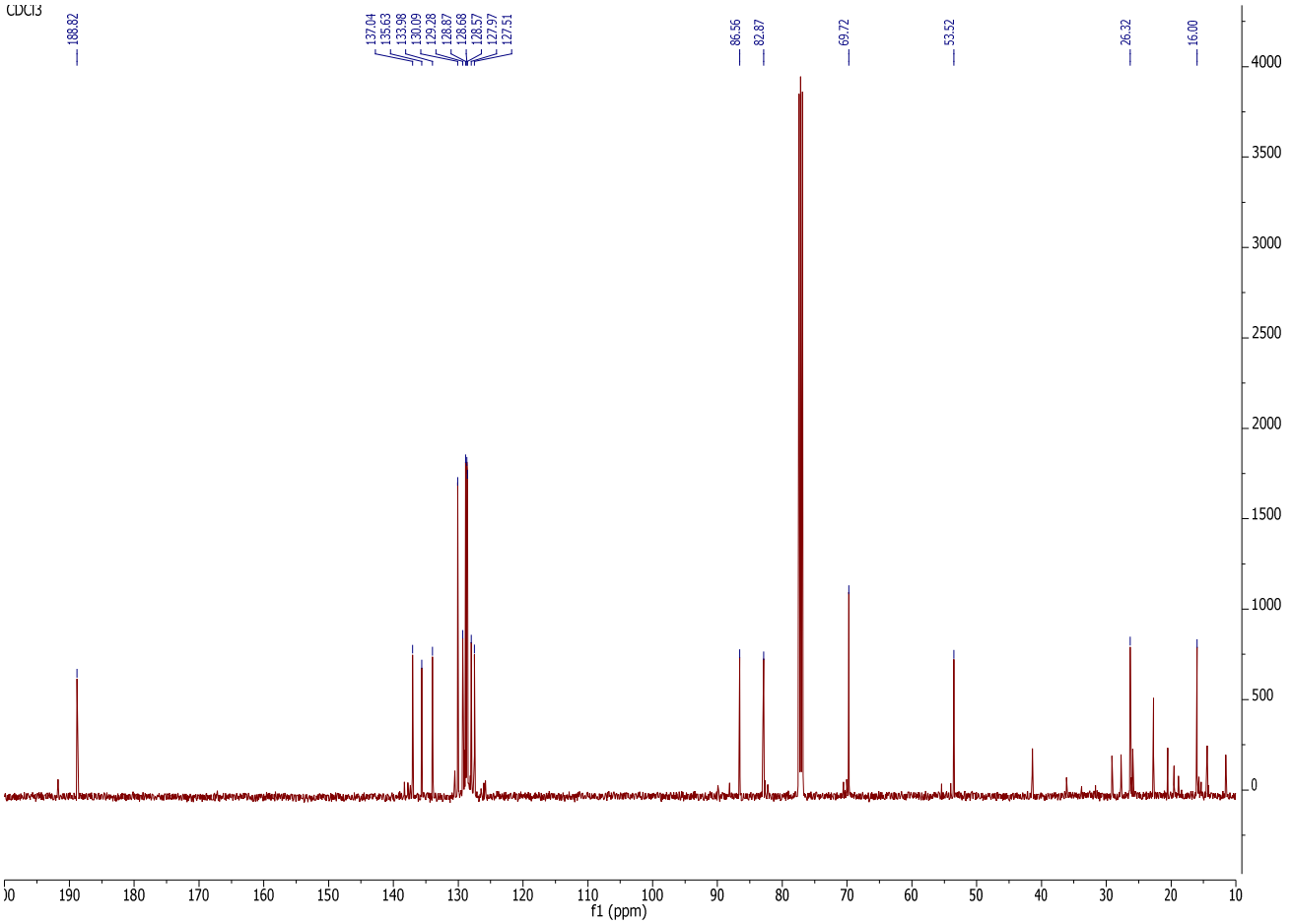

CDCl3
f2 (ppm)
f1 (ppm)


CDCl3
f2 (ppm)
f1 (ppm)


HO
N
S
S

2e


CDCl3
7.33
7.31
7.29
7.28
7.25
5.86
5.84
4.53
4.50
4.47
4.30
4.29
4.24
4.10
4.08
2.38
2.35
2.29
2.28
2.25
2.18
2.16
2.15
2.14
2.07
1.99
1.98
1.98
11.22
1.07
1.08
1.09
1.00
2.19
2.14
1.03
f1 (ppm)


CDCl3
188.82
137.04
135.63
133.98
130.09
129.28
128.87
128.68
128.57
127.97
127.51
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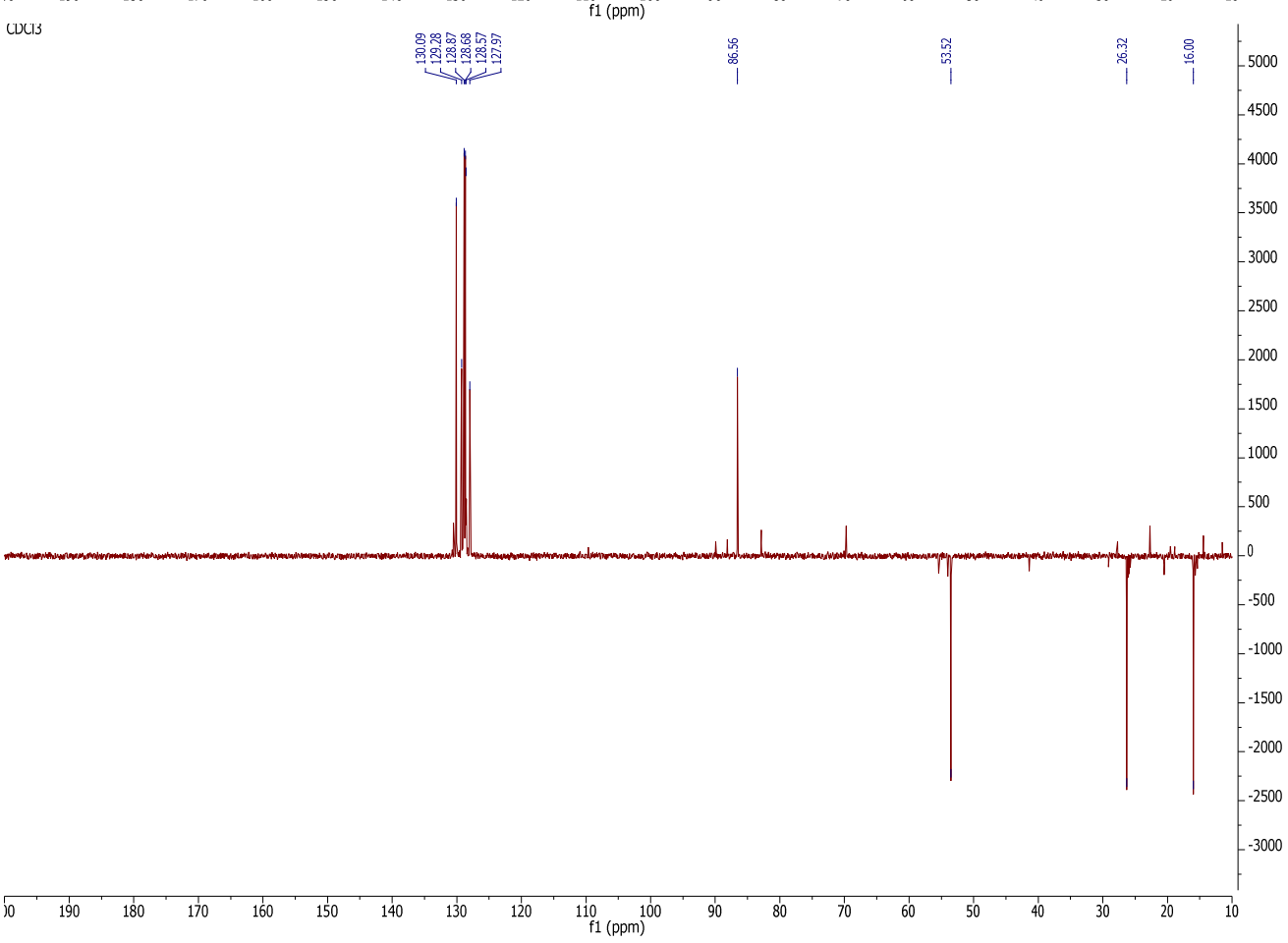
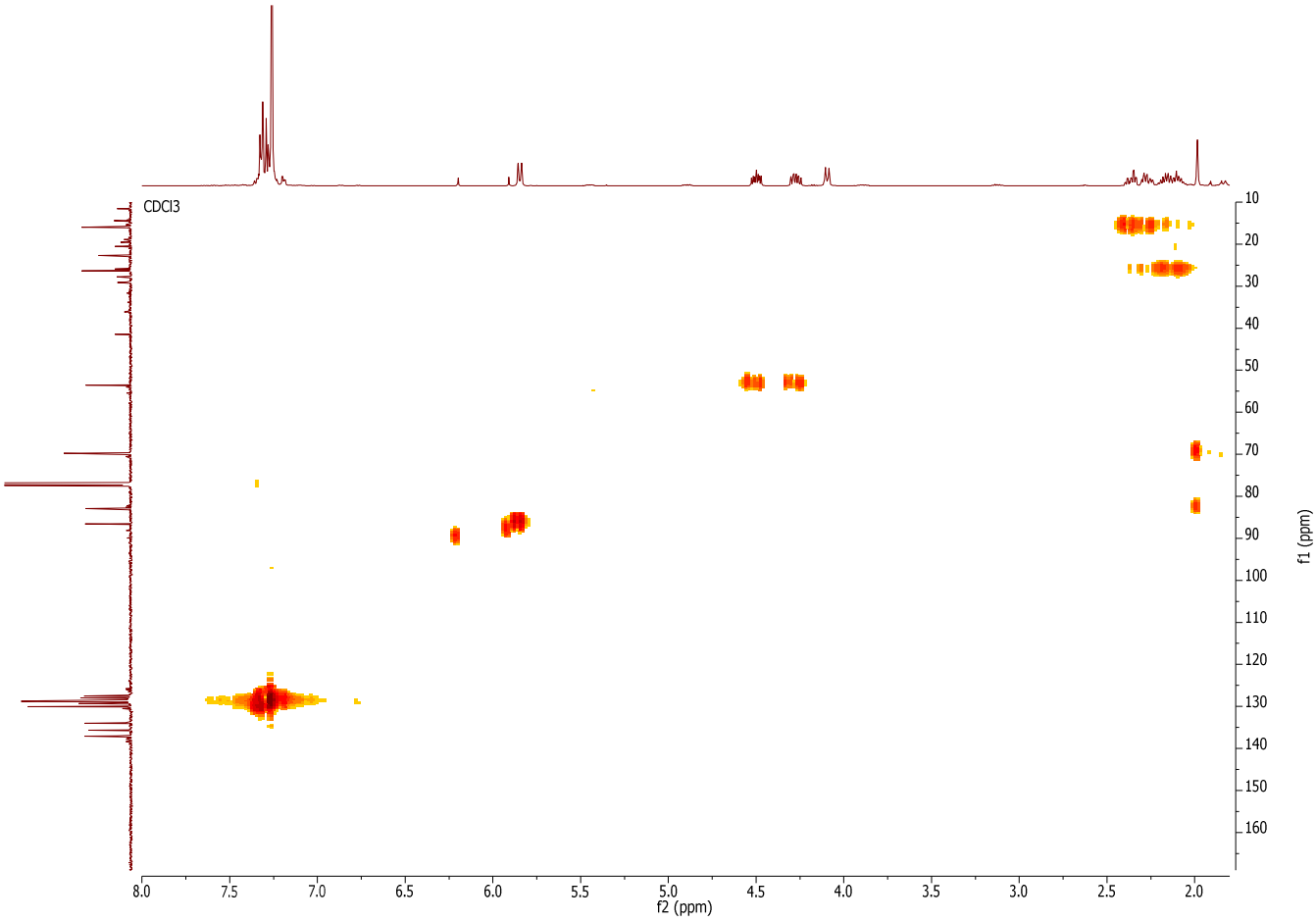
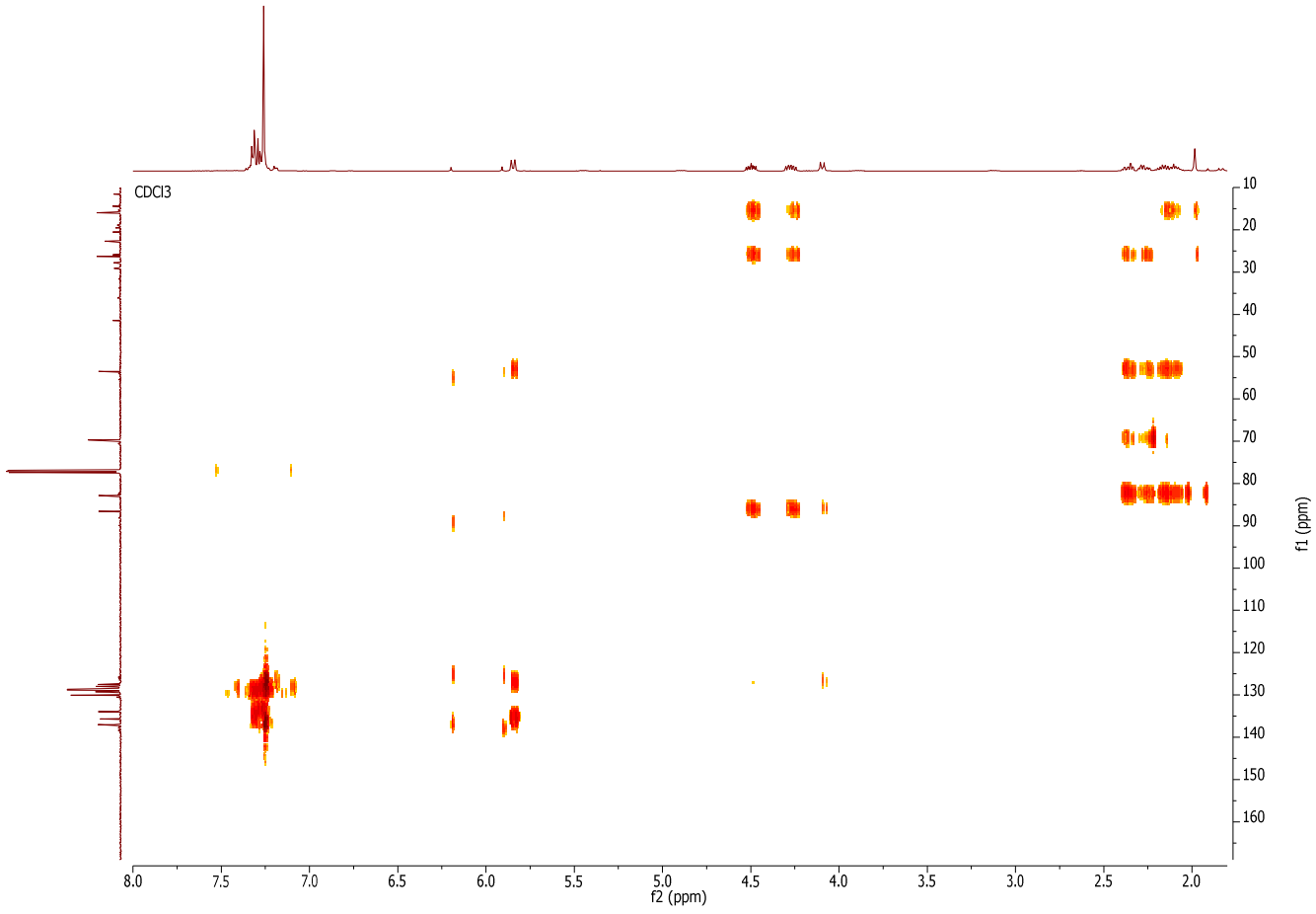
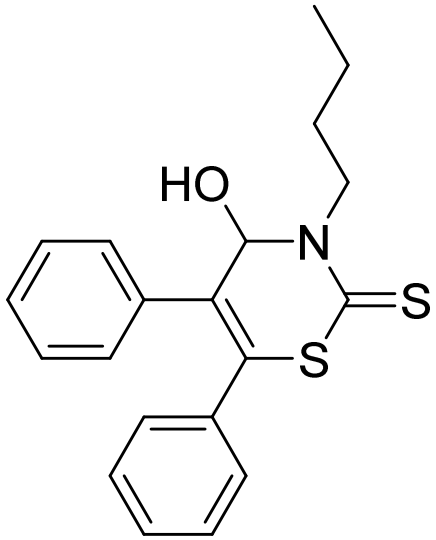
82.87
69.72
53.52
26.32
16.00
f1 (ppm)

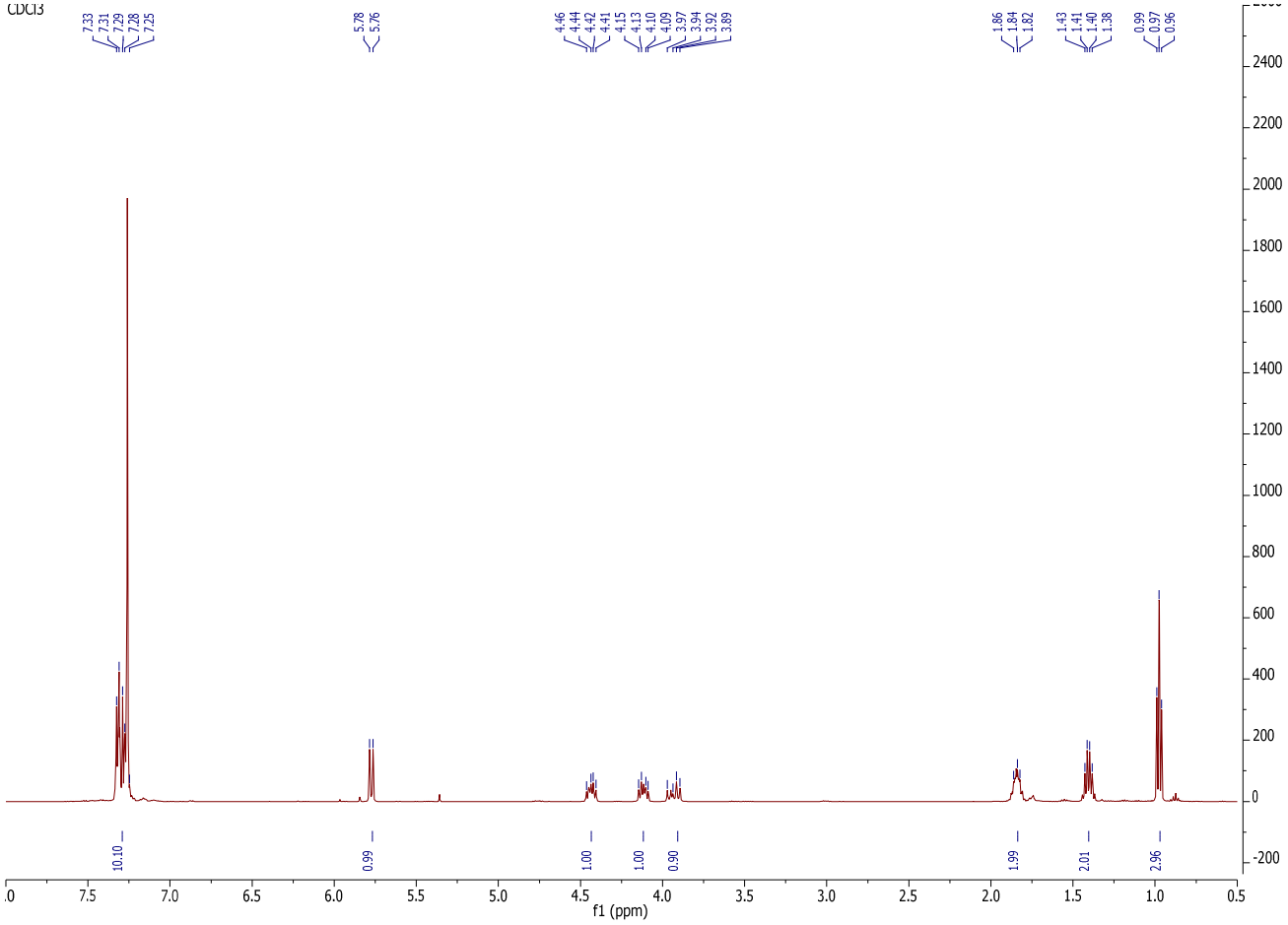

CDCl3
130.09
129.28
128.87
128.68
128.57
127.97
86.56
53.52
26.32
16.00
f1 (ppm)


CDCl3
f2 (ppm)
f1 (ppm)


CDCl3
f2 (ppm)
f1 (ppm)


HO
N
S
S

2f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7.29
7.28
7.25
5.78
5.76
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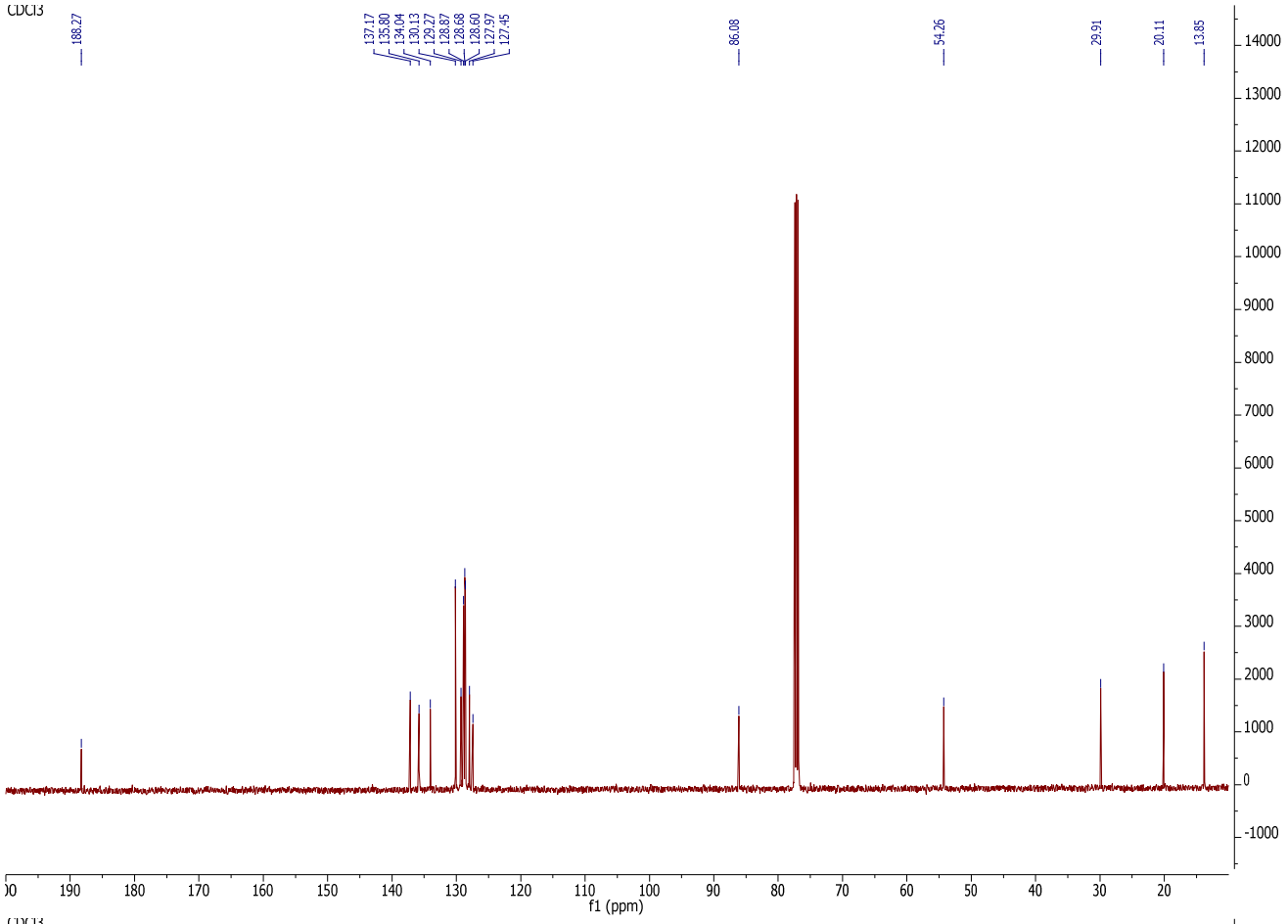
4.44
4.42
4.41
4.15
4.13
4.10
4.09
3.97
3.94
3.92
3.89
1.86
1.84
1.82
1.43
1.41
1.40
1.38
0.99
0.97
0.96
10.10
0.99
1.00
1.00
0.90
1.99
2.01
2.96
f1 (ppm)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134.04
130.13
129.27
128.87
128.68
128.60
127.97
127.45
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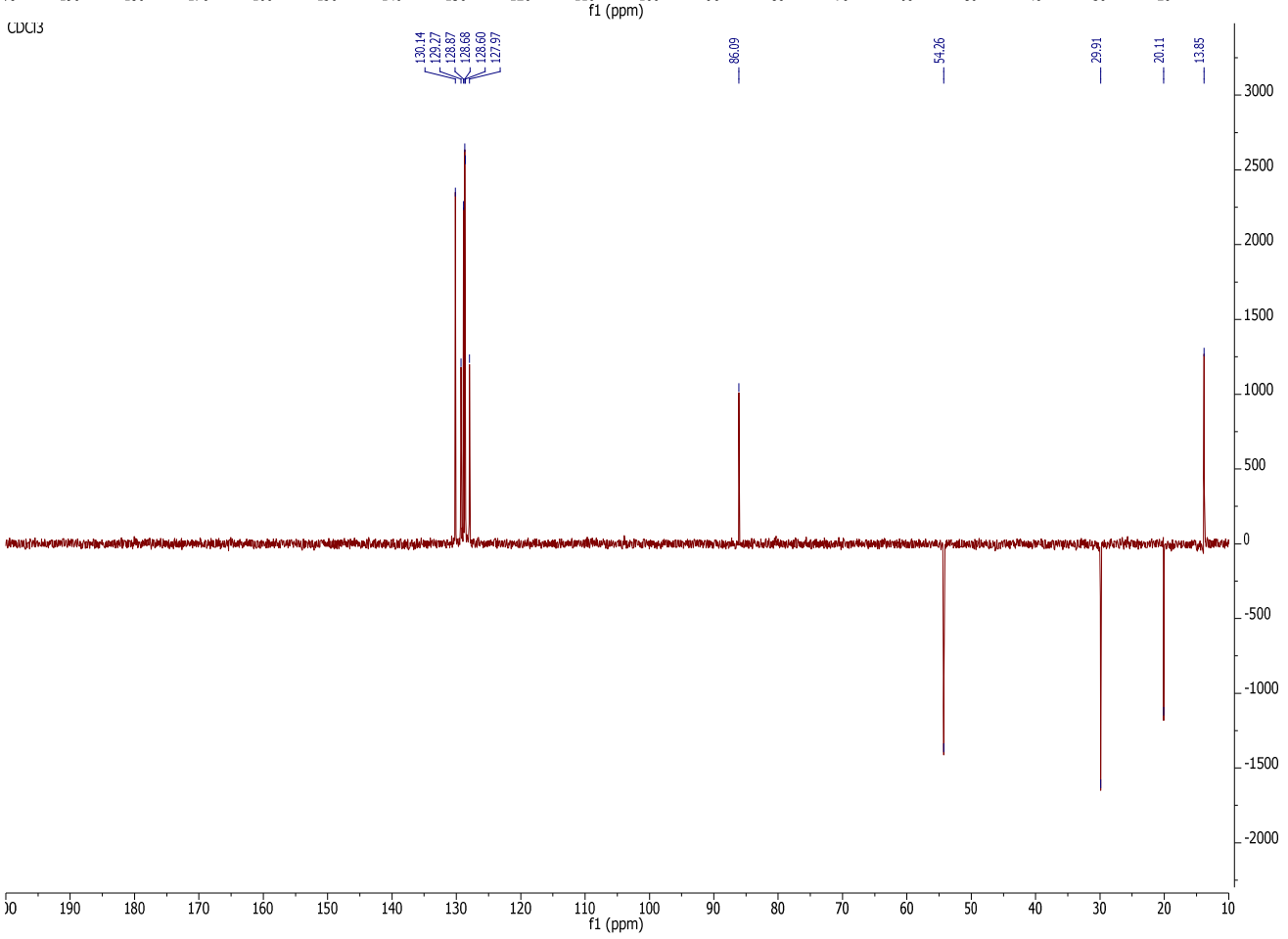
54.26
29.91
20.11
13.85
f1 (ppm)


CDCl3
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129.27
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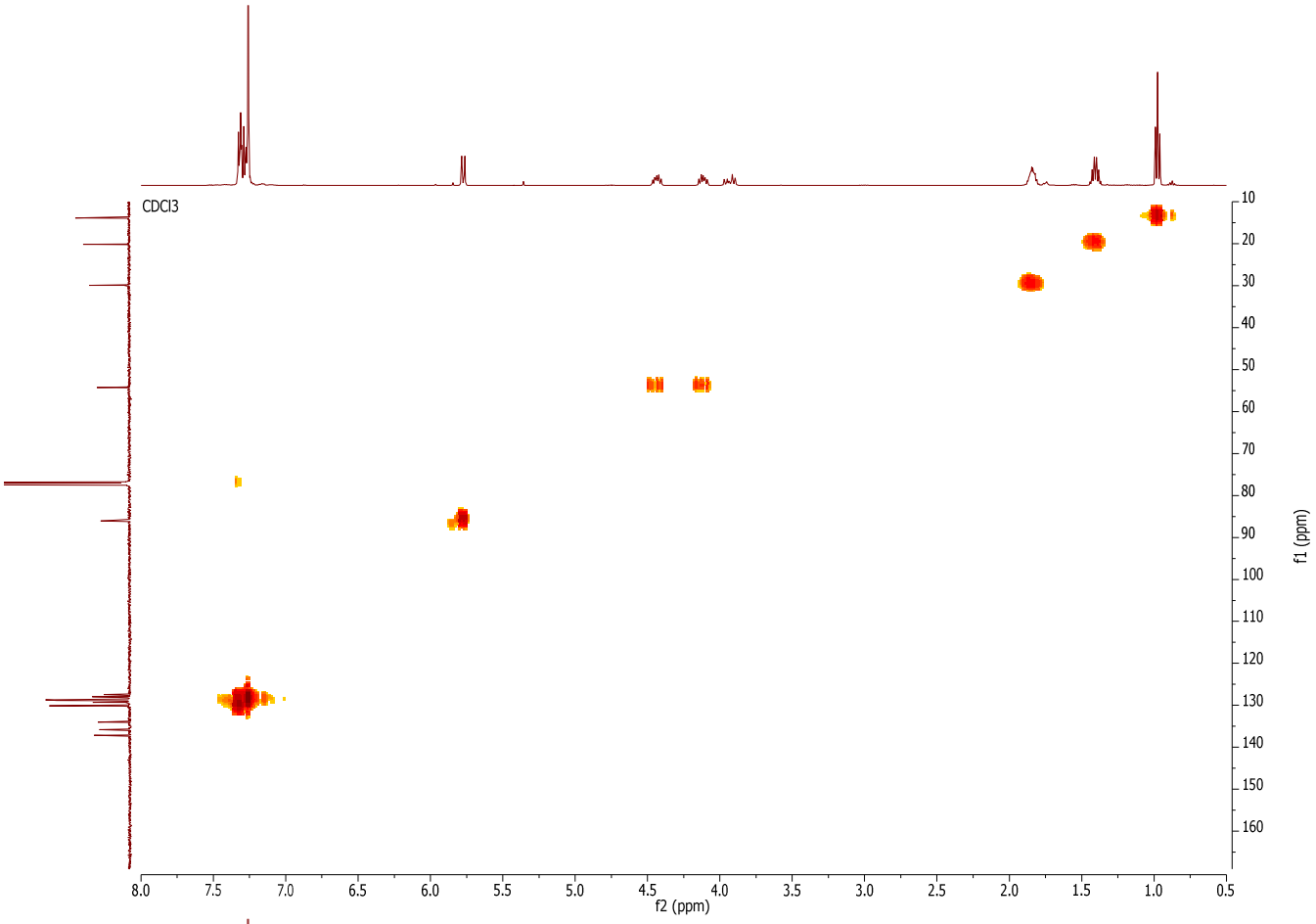
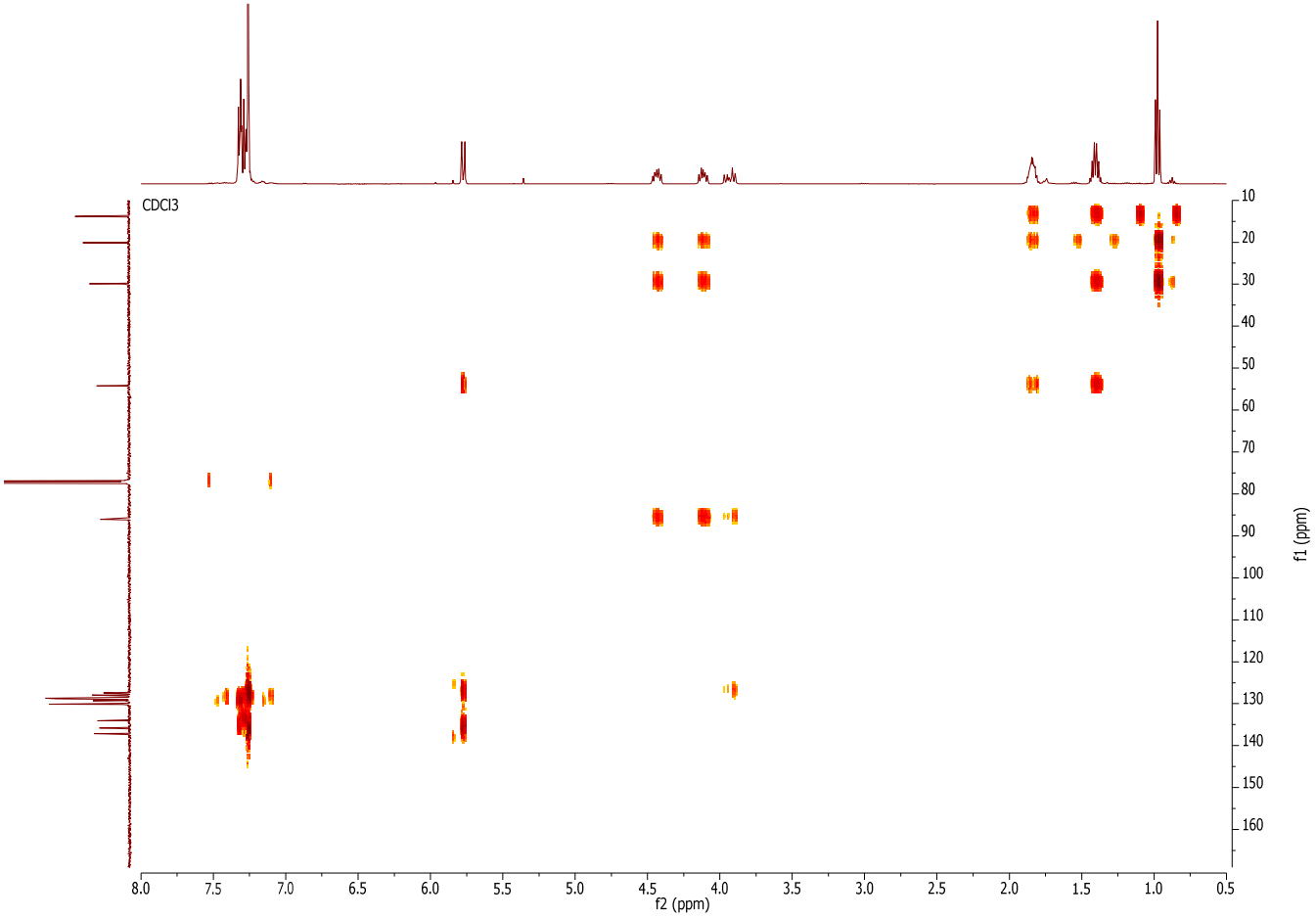
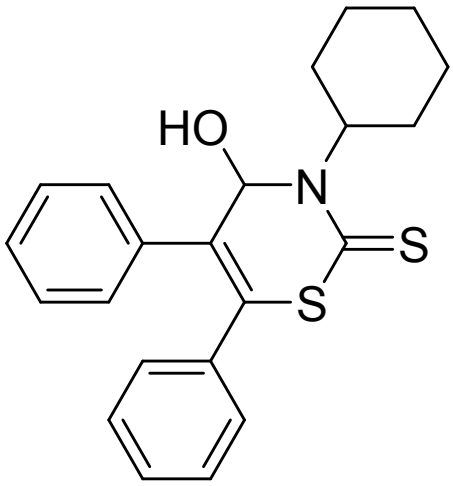
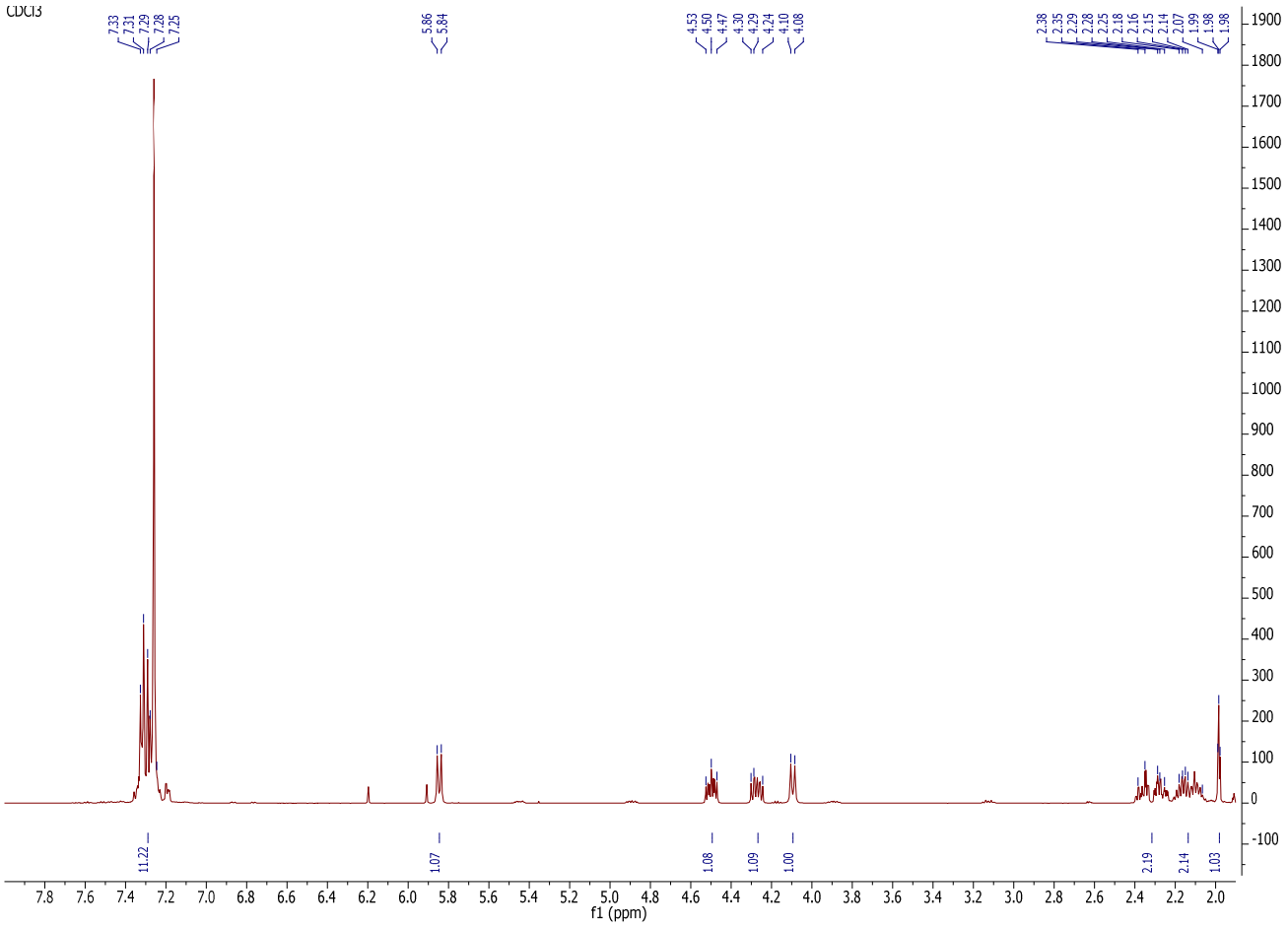
128.68
128.60
127.97
86.09
54.26
29.91
20.11
13.85
f1 (ppm)


CDCl3
f2 (ppm)
f1 (ppm)


CDCl3
f2 (ppm)
f1 (ppm)


HO
N
S
S

2g


CDCl3
7.33
7.31
7.29
7.28
7.25
5.86
5.84
4.53
4.50
4.47
4.30
4.29
4.24
4.10
4.08
2.38
2.35
2.29
2.28
2.25
2.18
2.16
2.15
2.14
2.07
1.99
1.98
1.98
11.22
1.07
1.08
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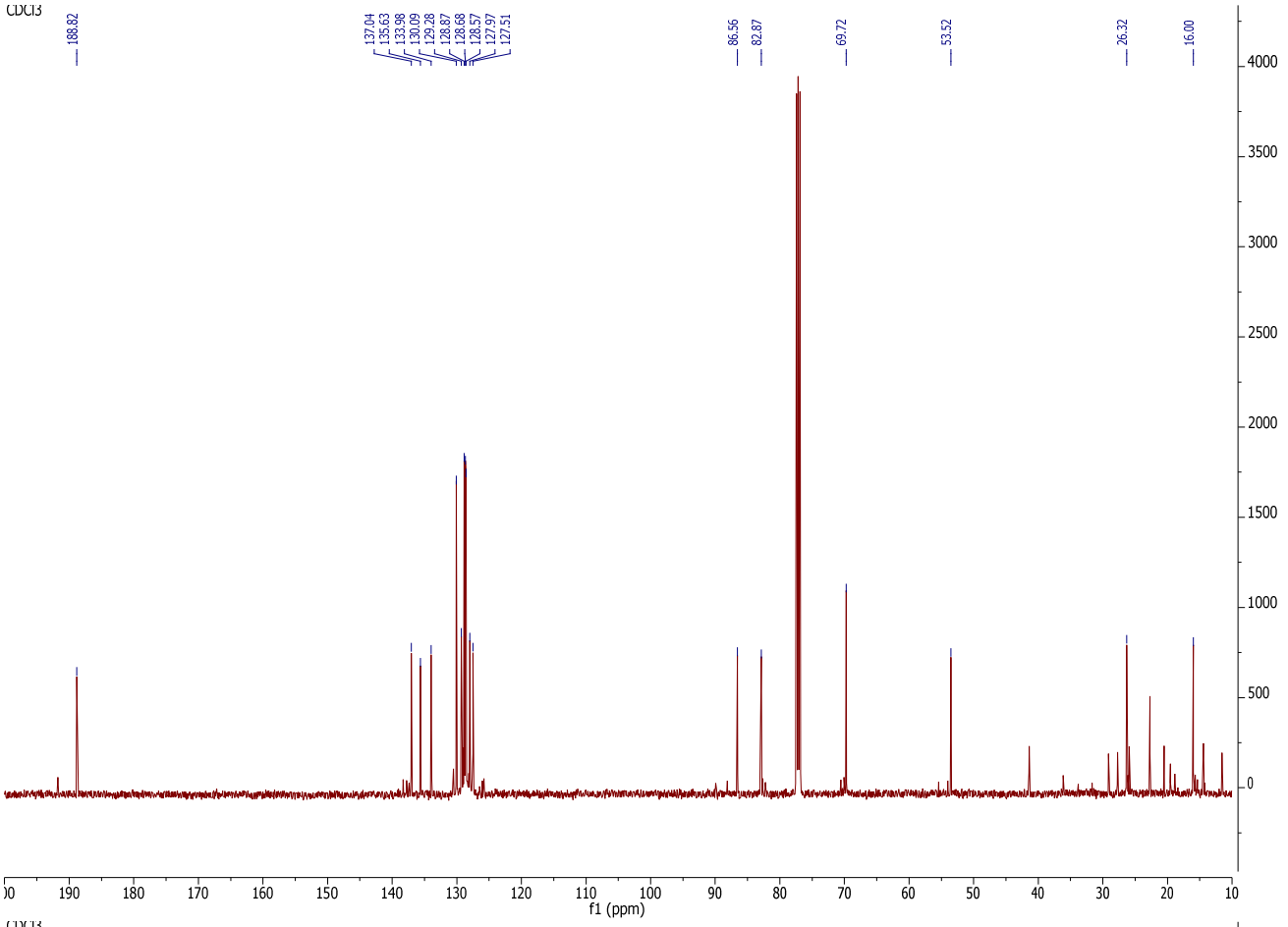
1.00
2.19
2.14
1.03
f1 (ppm)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135.63
133.98
130.09
129.28
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128.68
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127.97
127.51
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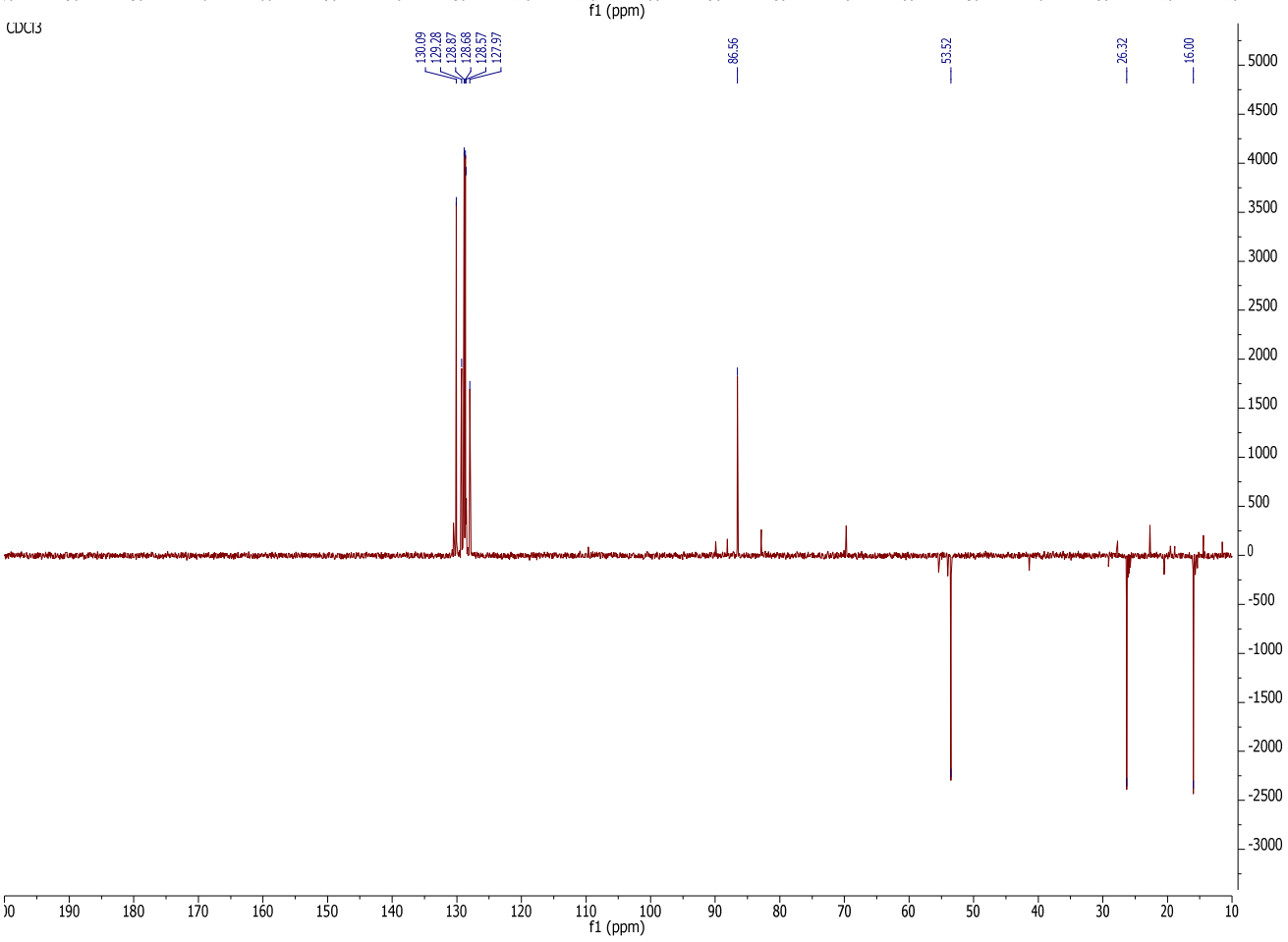
82.87
69.72
53.52
26.32
16.00
f1 (ppm)


CDCl3
130.09
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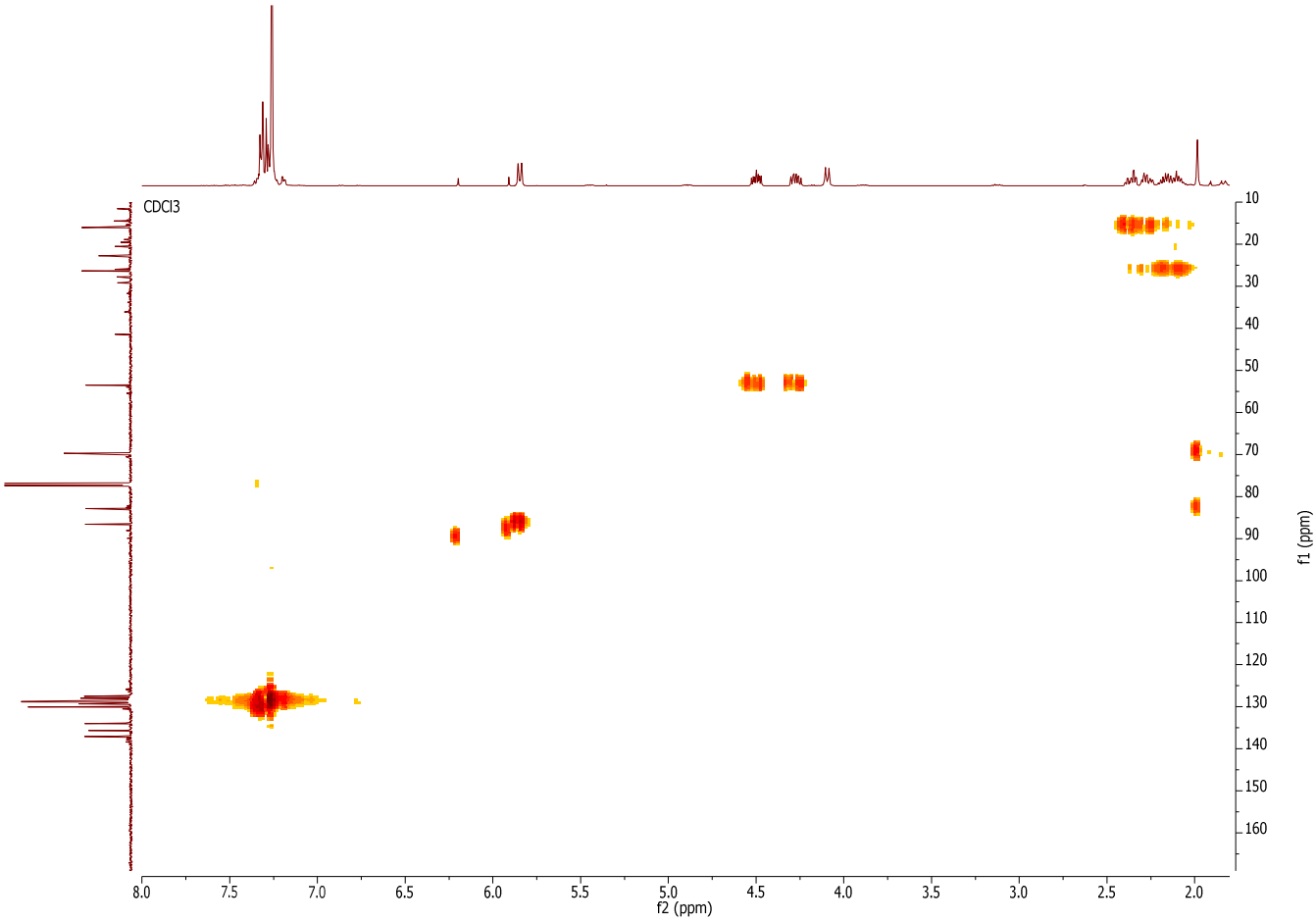
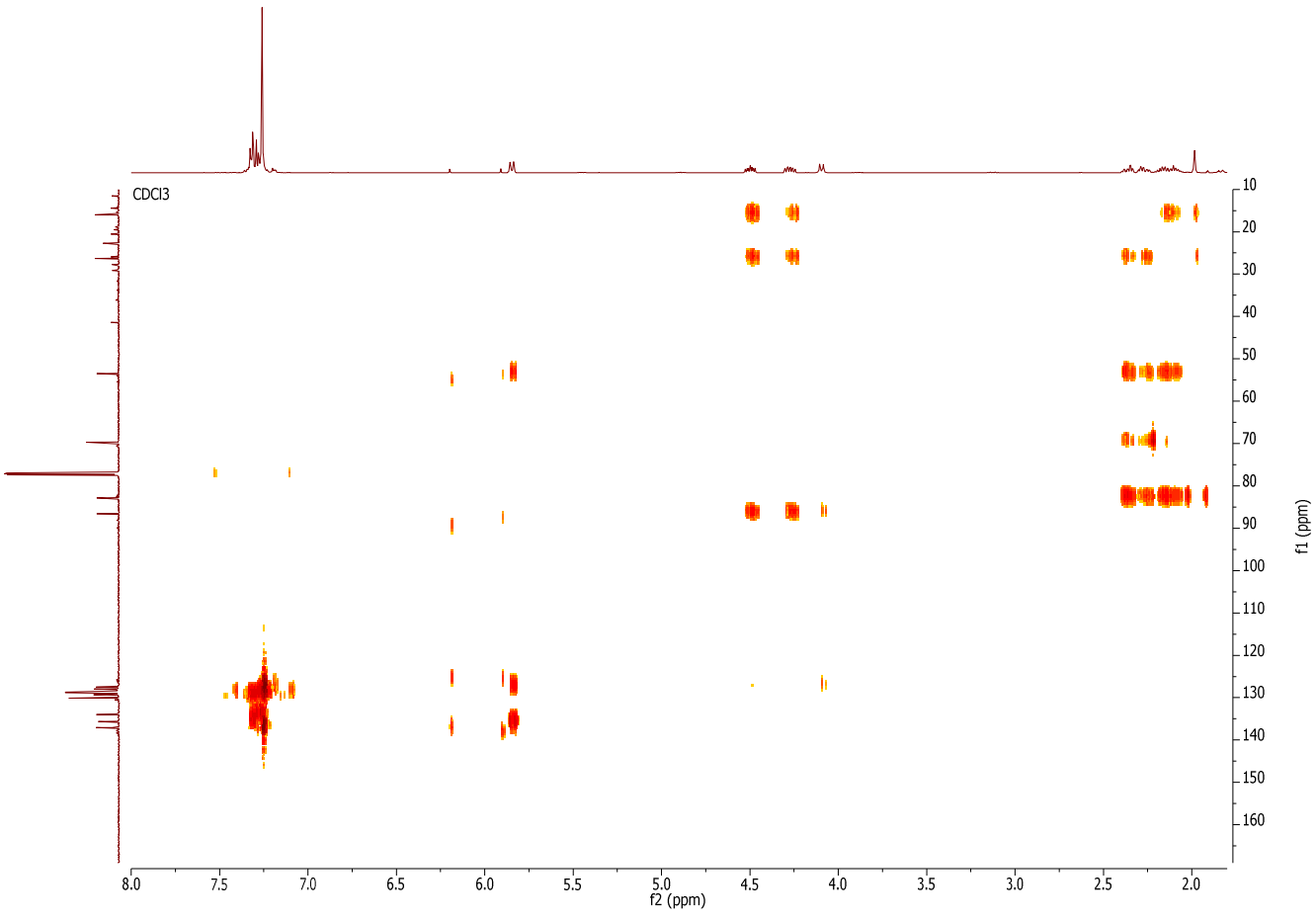
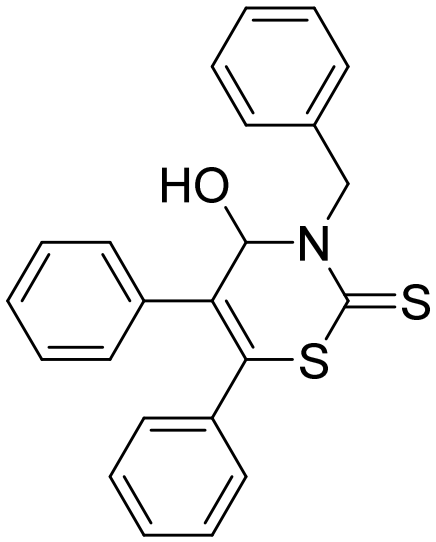
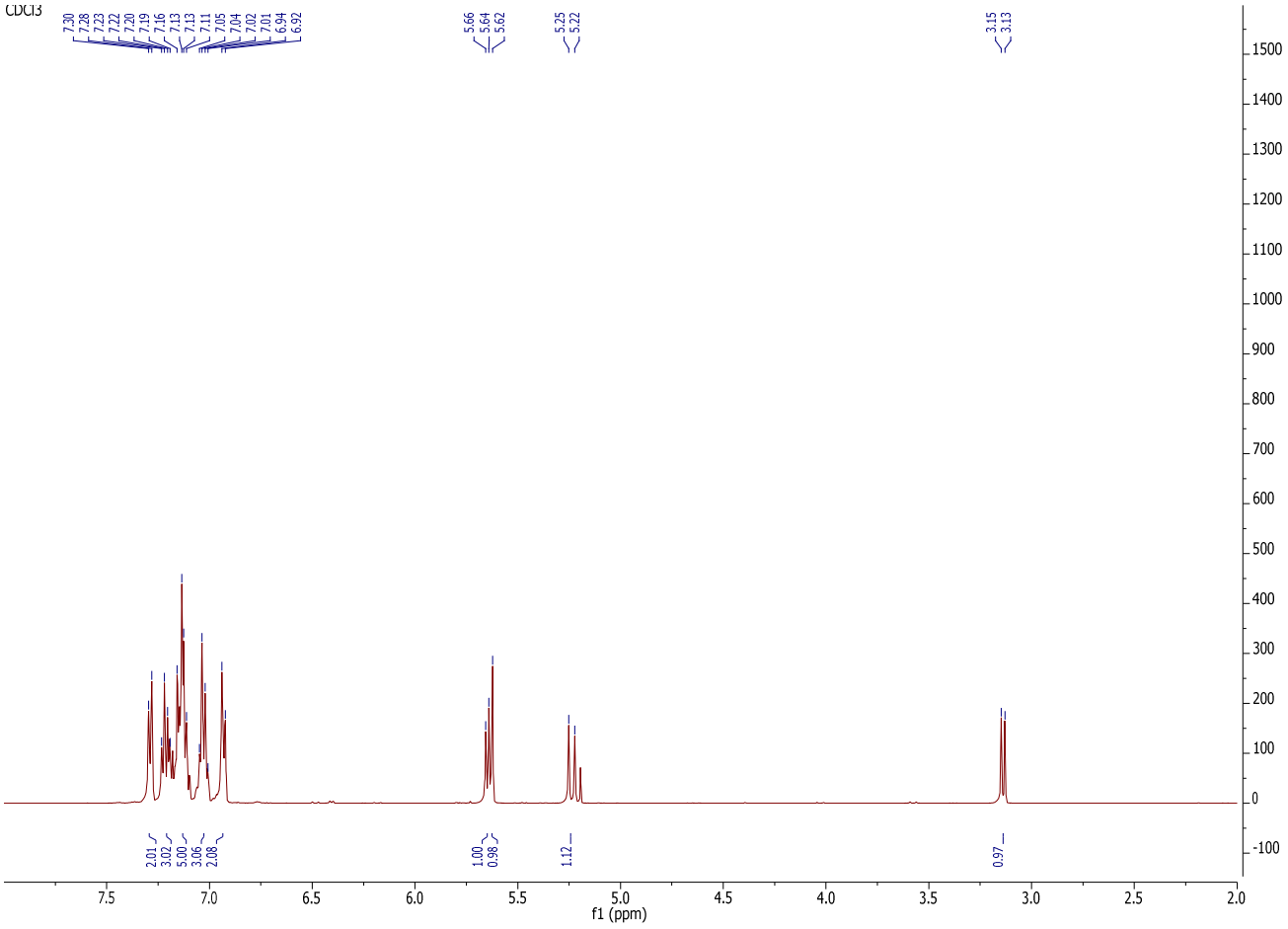
128.87
128.68
128.57
127.97
86.56
53.52
26.32
16.00
f1 (ppm)


CDCl3
f2 (ppm)
f1 (ppm)


CDCl3
f2 (ppm)
f1 (ppm)


HO
N
S
S

2h


CDCl3
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7.23
7.22
7.20
7.19
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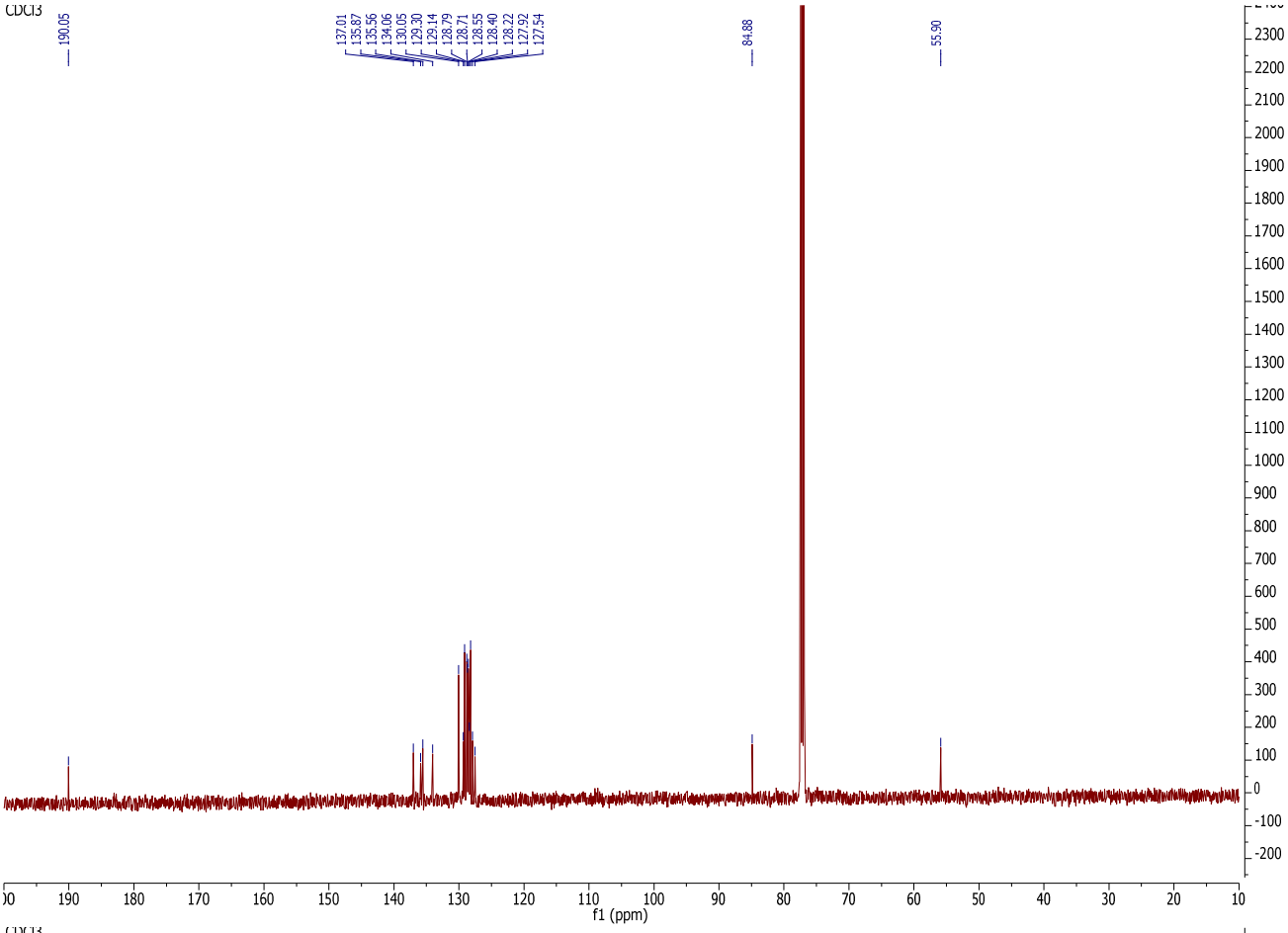
7.13
7.13
7.11
7.05
7.04
7.02
7.01
6.94
6.92
5.66
5.64
5.62
5.25
5.22
3.15
3.13
2.01
3.02
5.00
3.06
2.08
1.00
0.98
1.12
0.97
f1 (ppm)


CDCl3
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135.87
135.56
134.06
130.05
129.30
129.14
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128.71
128.55
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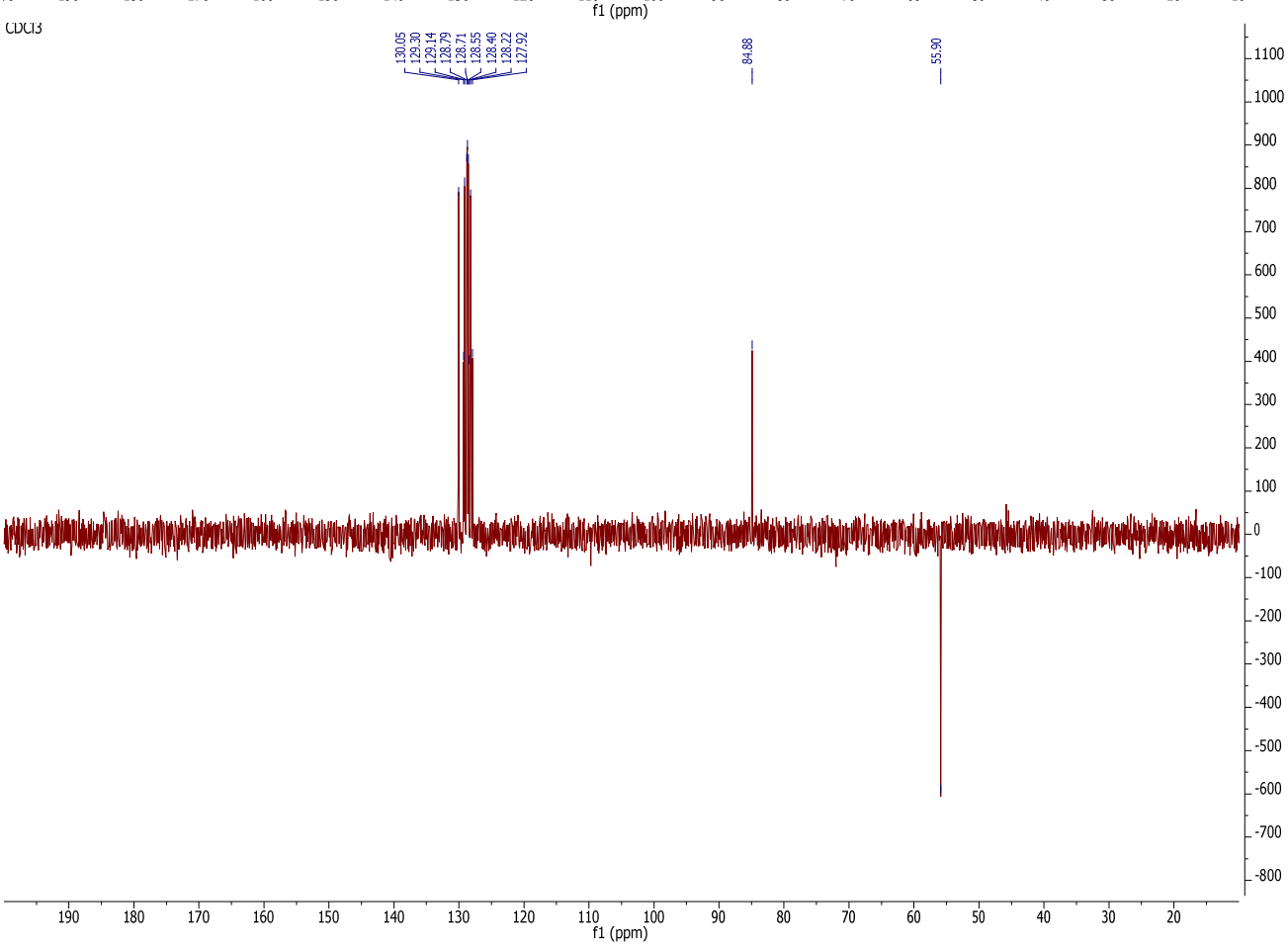
128.22
127.92
127.54
84.88
55.90
f1 (ppm)


CDCl3
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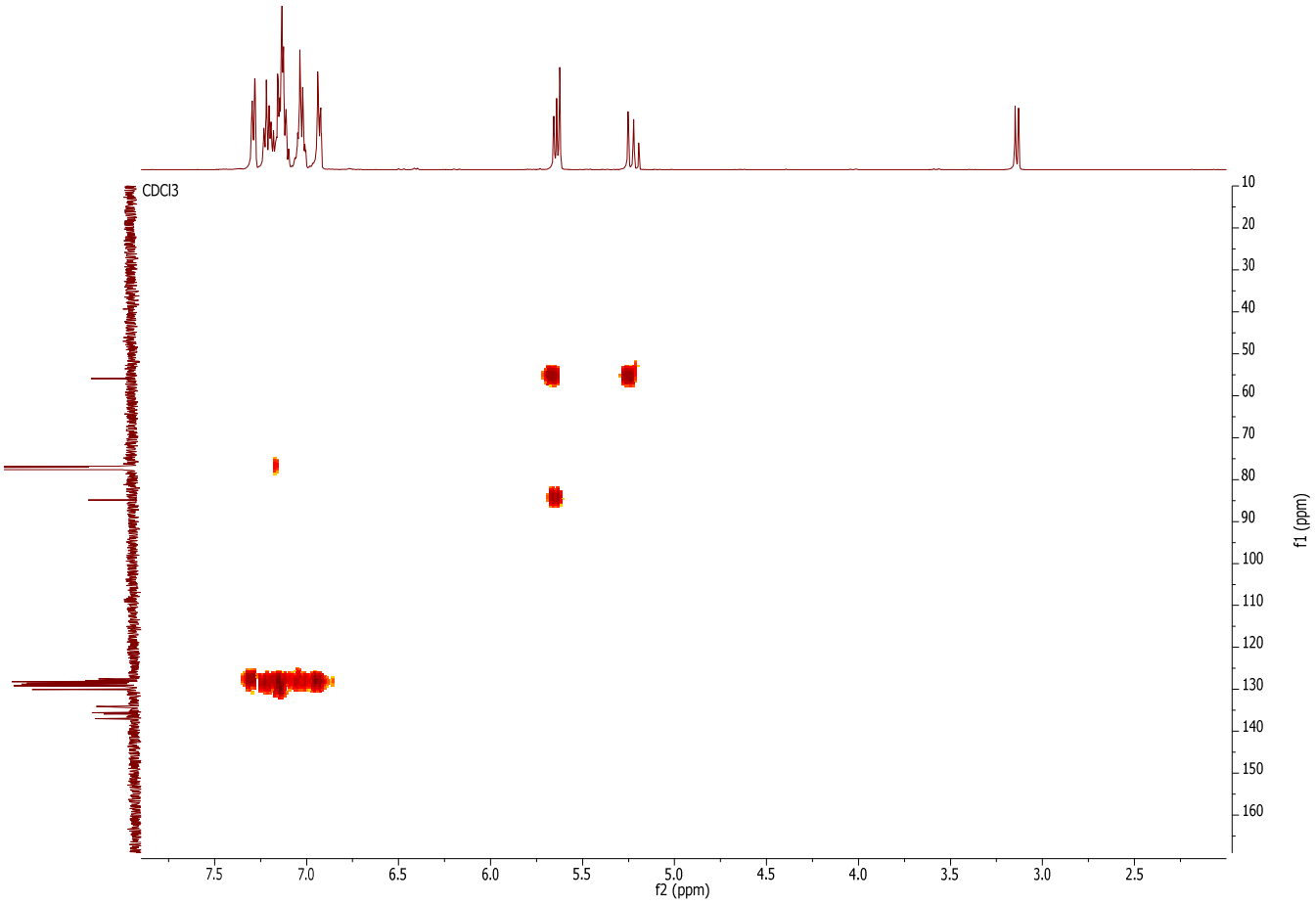
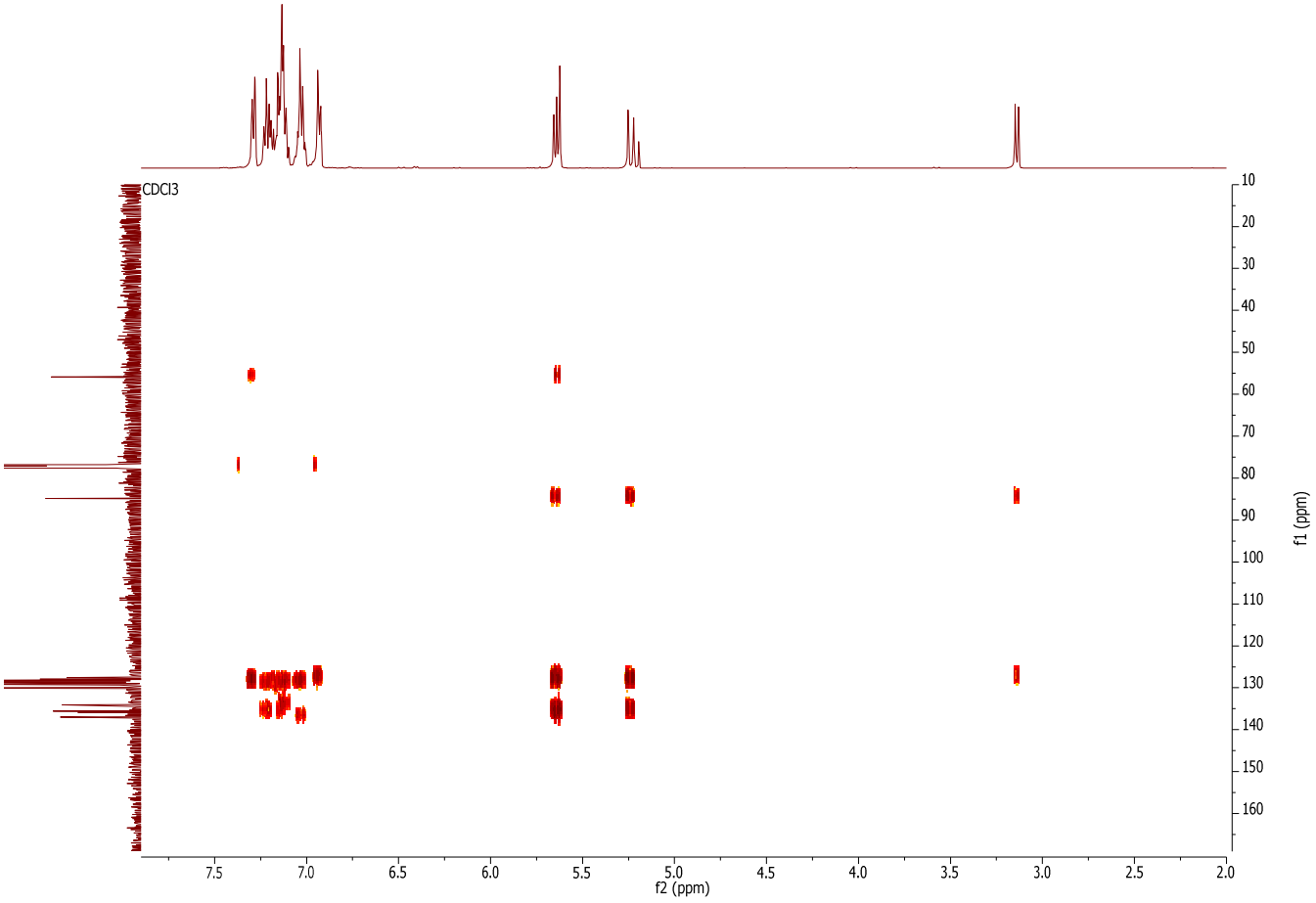
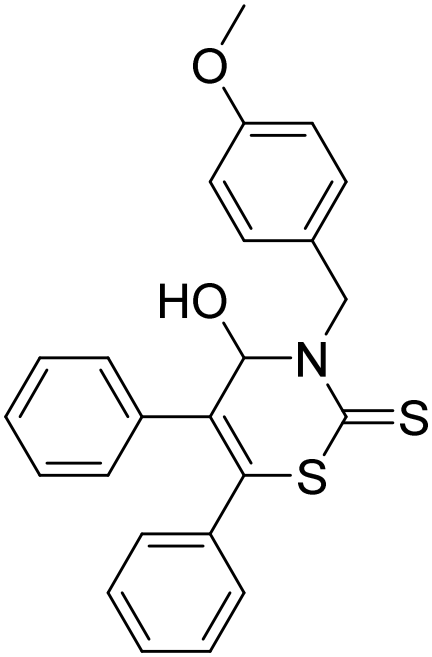
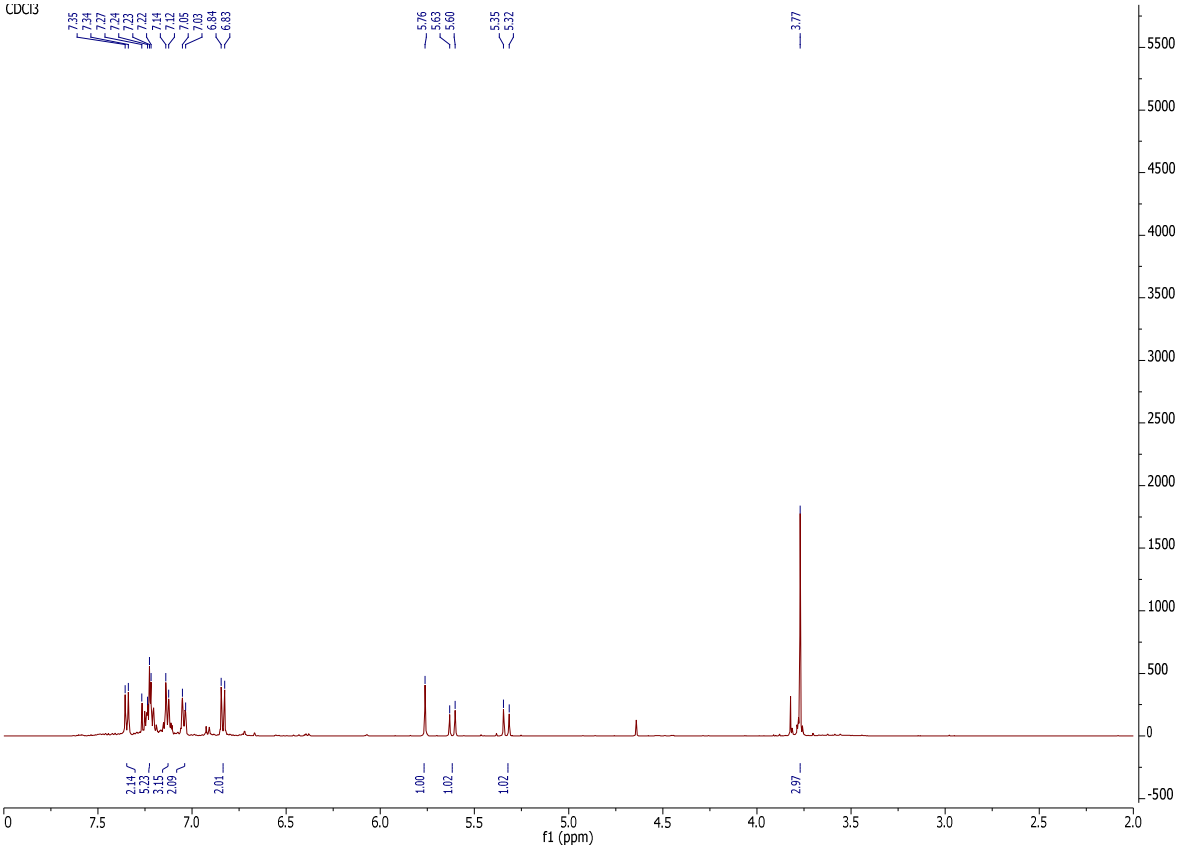
129.30
129.14
128.79
128.71
128.55
128.40
128.22
127.92
84.88
55.90
f1 (ppm)

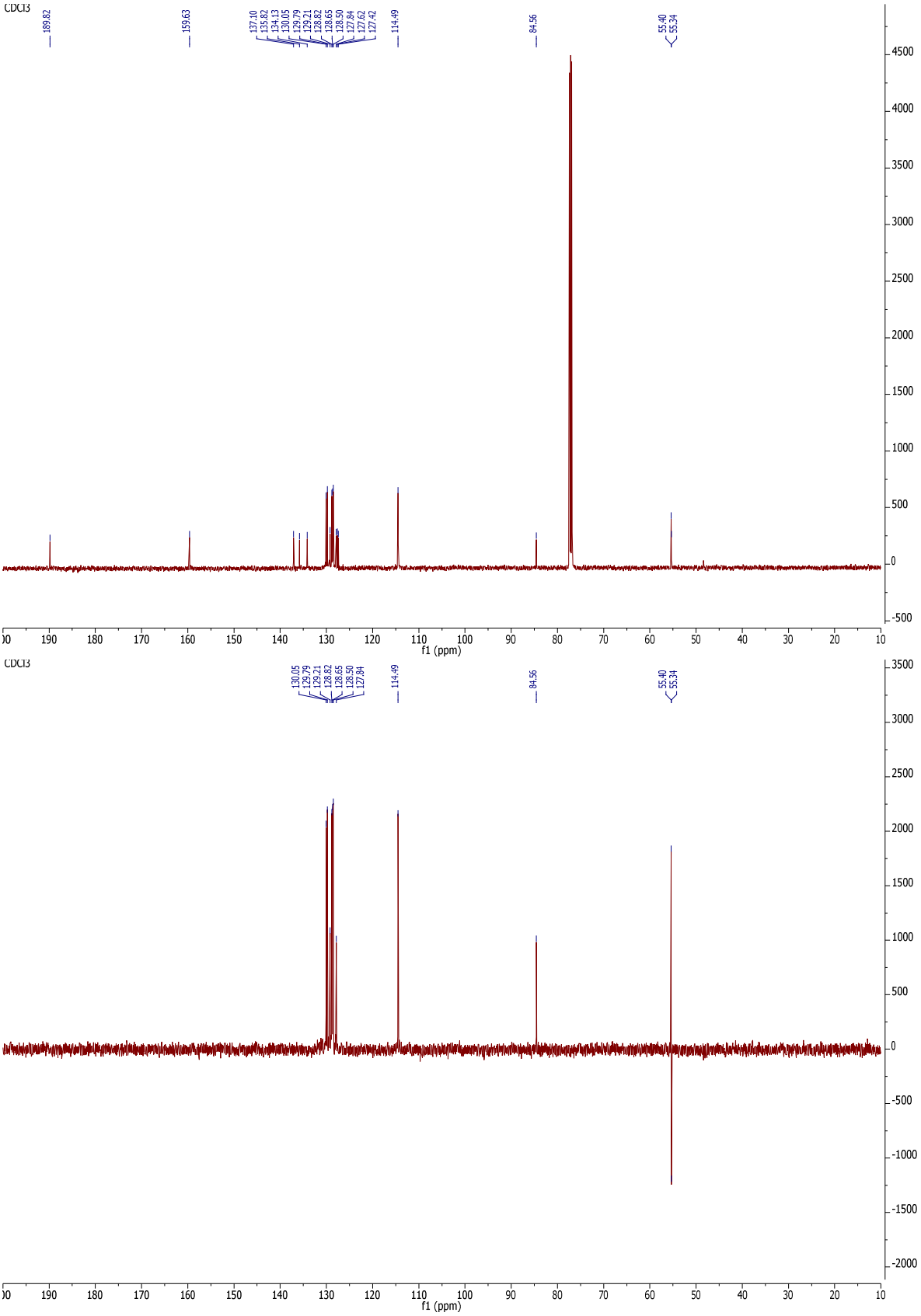

CDCl3
f2 (ppm)
f1 (ppm)


CDCl3
f2 (ppm)
f1 (ppm)


O
HO
N
S
S

2i


CDCl3
7.35
7.34
7.27
7.24
7.23
7.22
7.14
7.12
7.05
7.03
6.84
6.83
5.76
5.63
5.60
5.35
5.32
3.77
2.14
5.23
3.15
2.09
2.01
1.00
1.02
1.02
2.97
f1 (ppm)


CDCl3
189.82
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137.10
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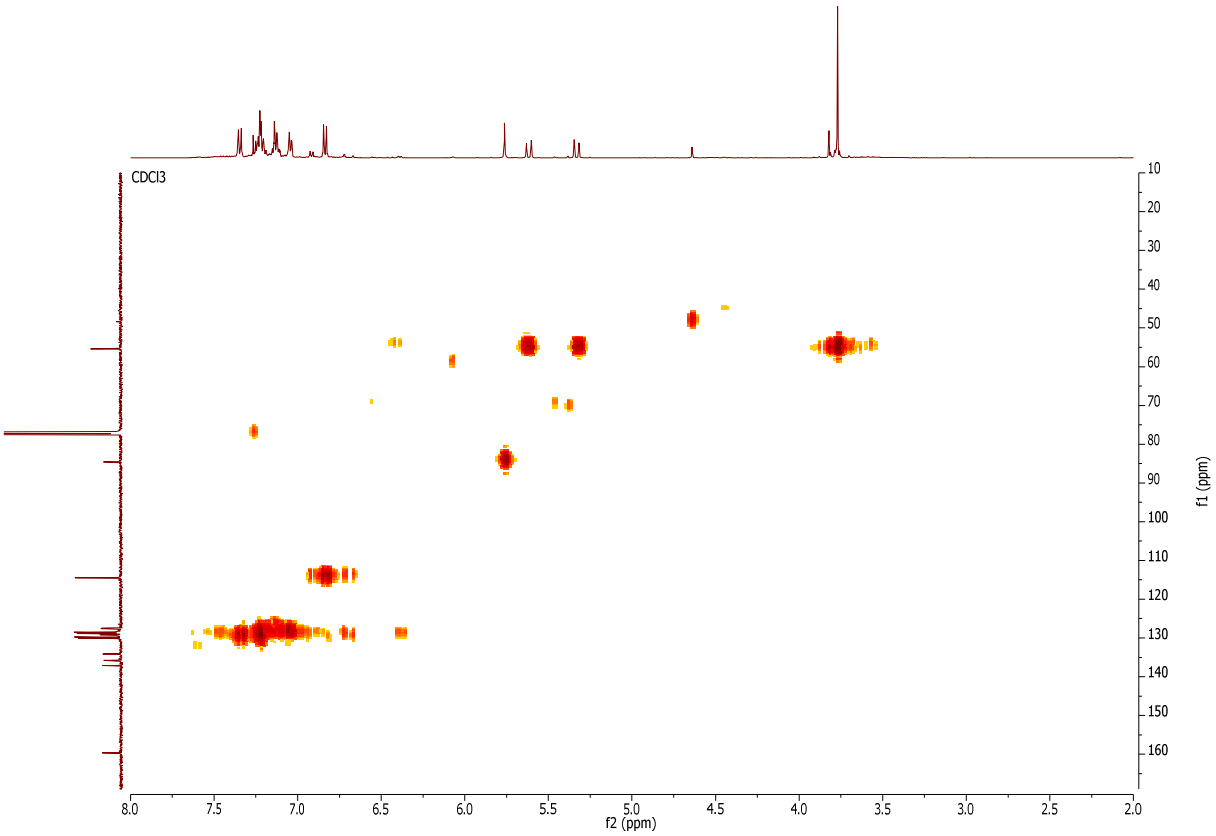
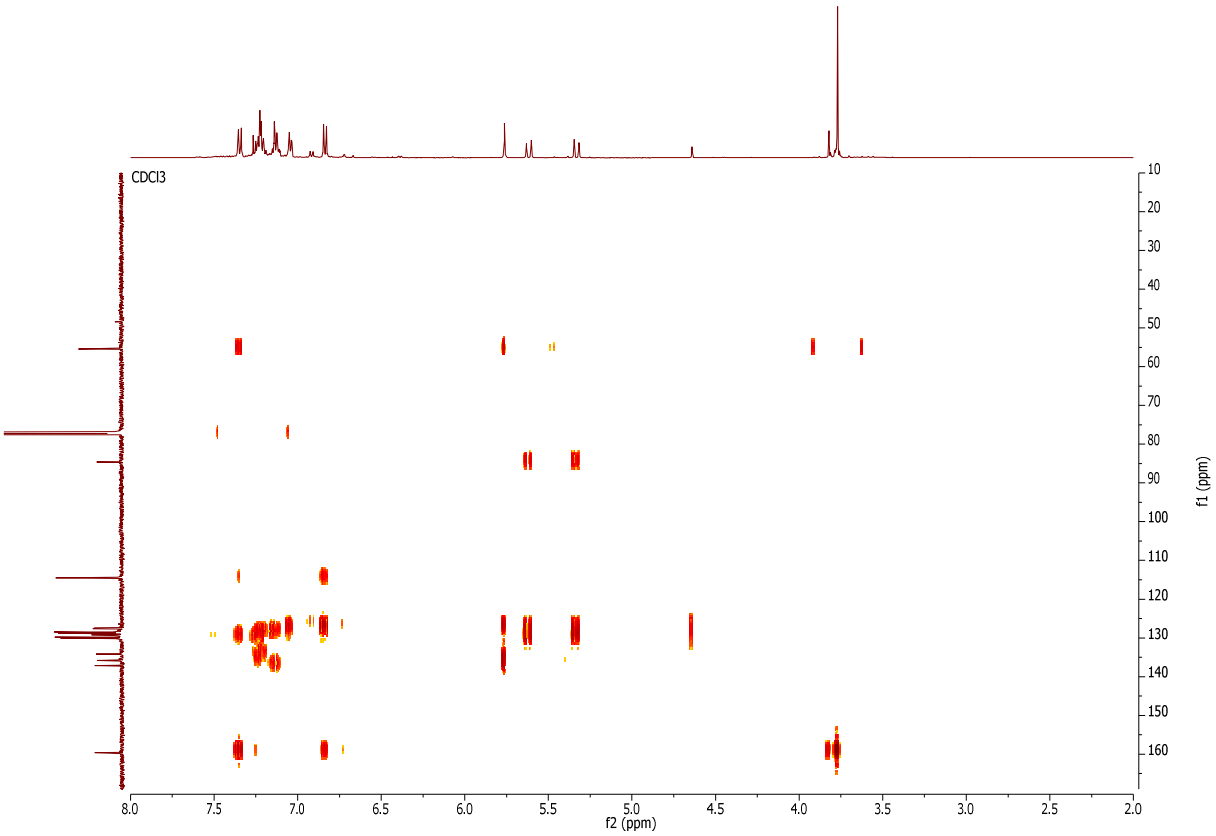
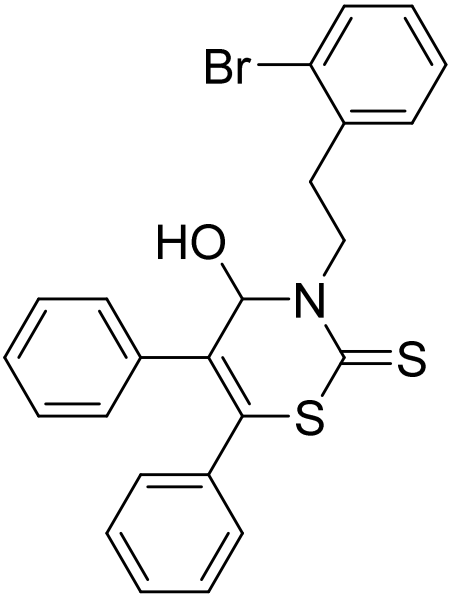
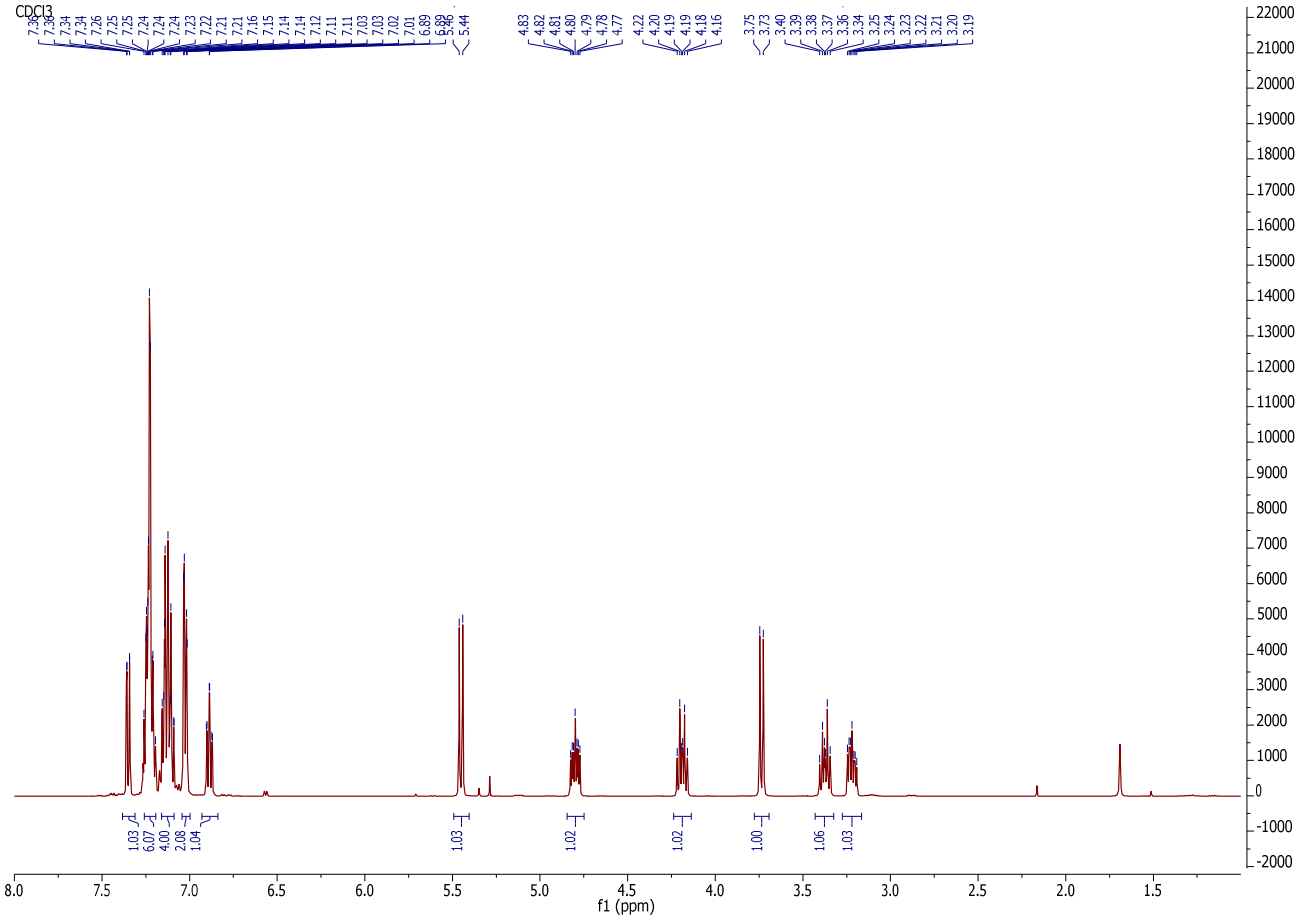
134.13
130.05
129.79
129.21
128.82
128.65
128.50
127.84
127.62
127.42
114.49
84.56
55.40
55.34
f1 (ppm)
CDCl3
130.05
129.79
129.21
128.82
128.65
128.50
127.84
114.49
84.56
55.40
55.34
f1 (ppm)

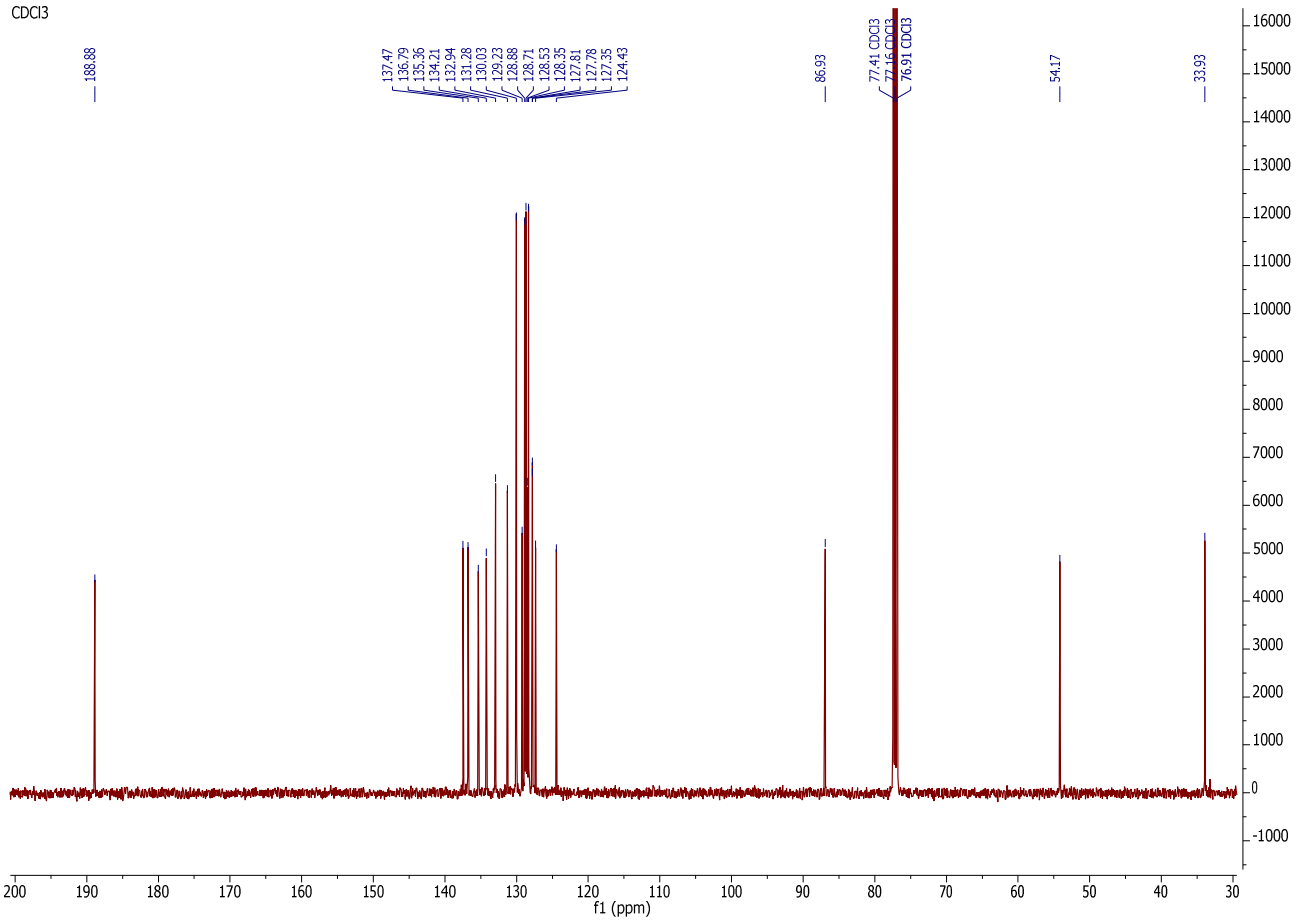

CDCl3
f2 (ppm)
f1 (ppm)


CDCl3
f2 (ppm)
f1 (ppm)



2j

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134.21
132.94
131.28
130.03
129.23
128.88
128.71
128.53
128.35
127.81
127.78
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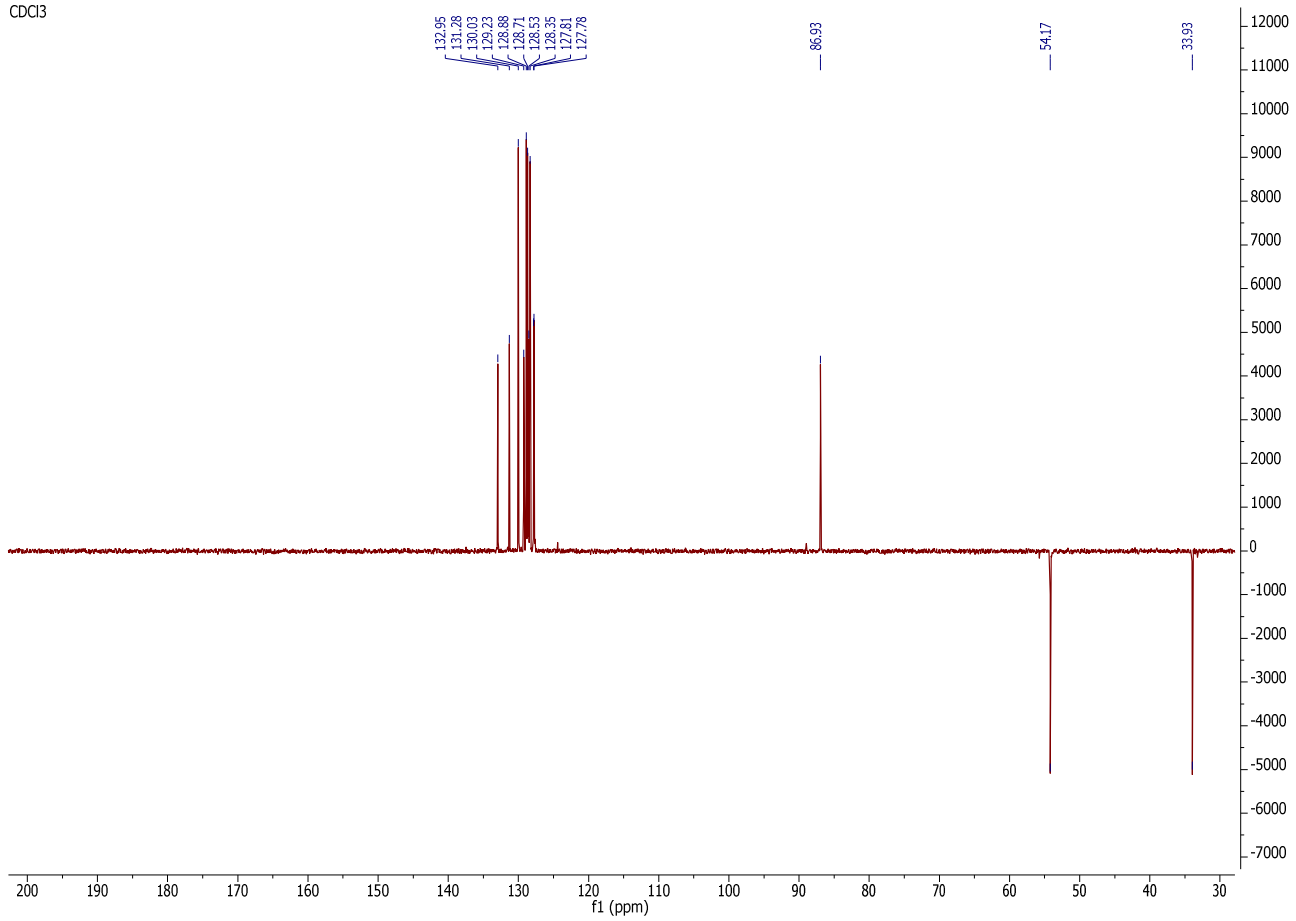
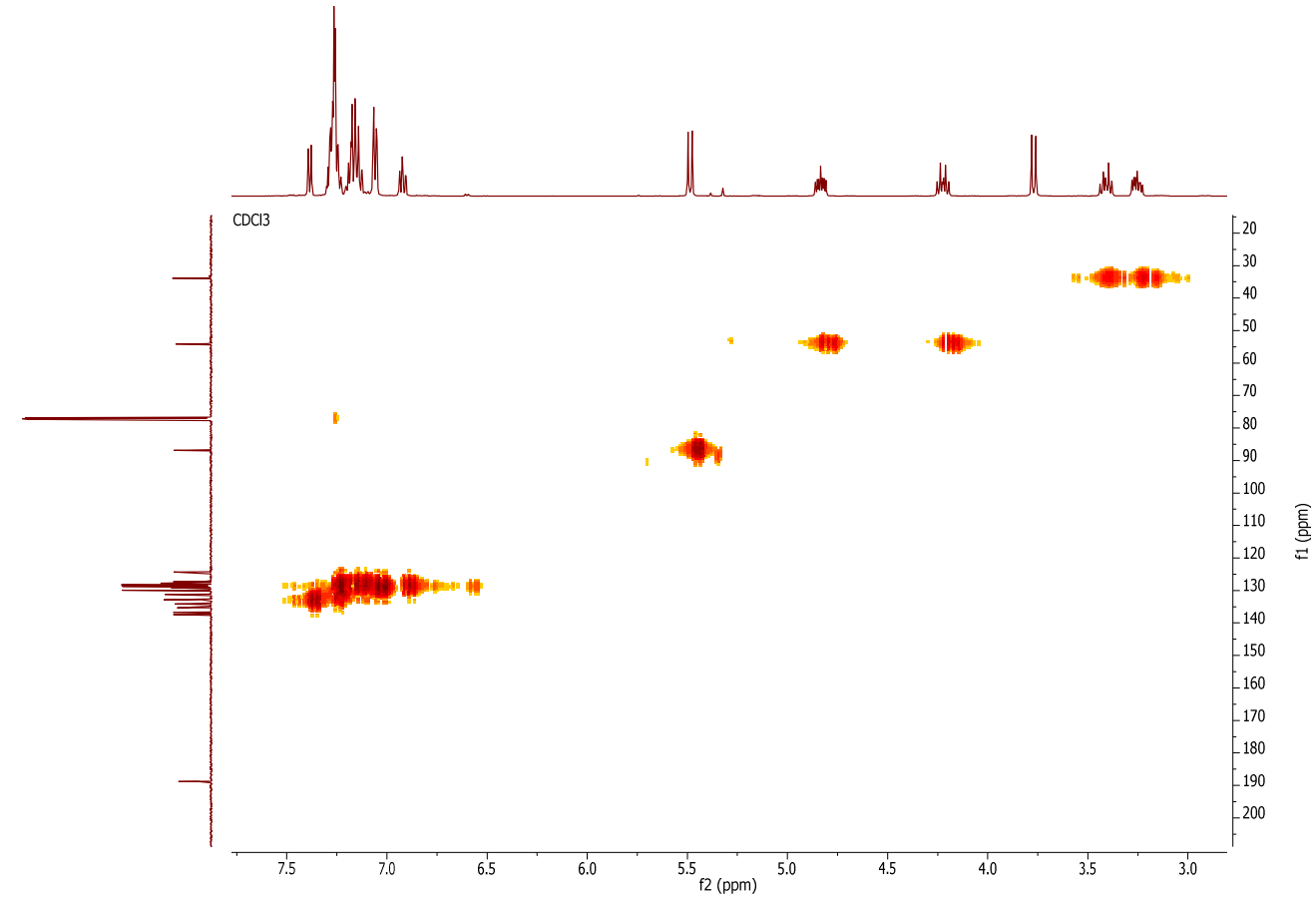
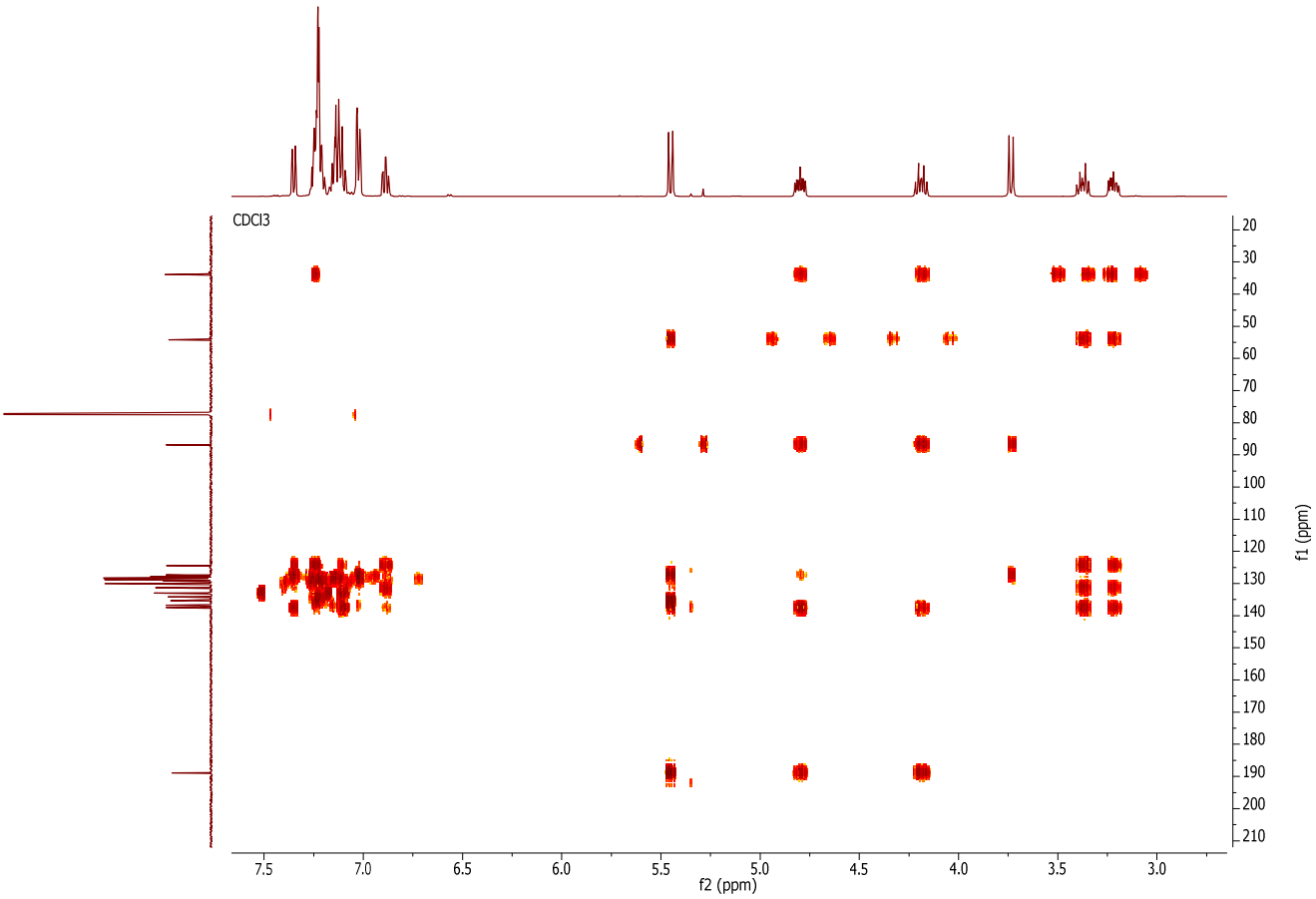
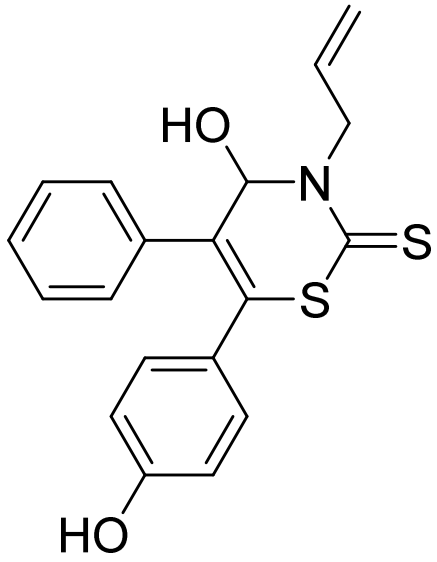
124.43
86.93
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
54.17
33.93
f1 (ppm)

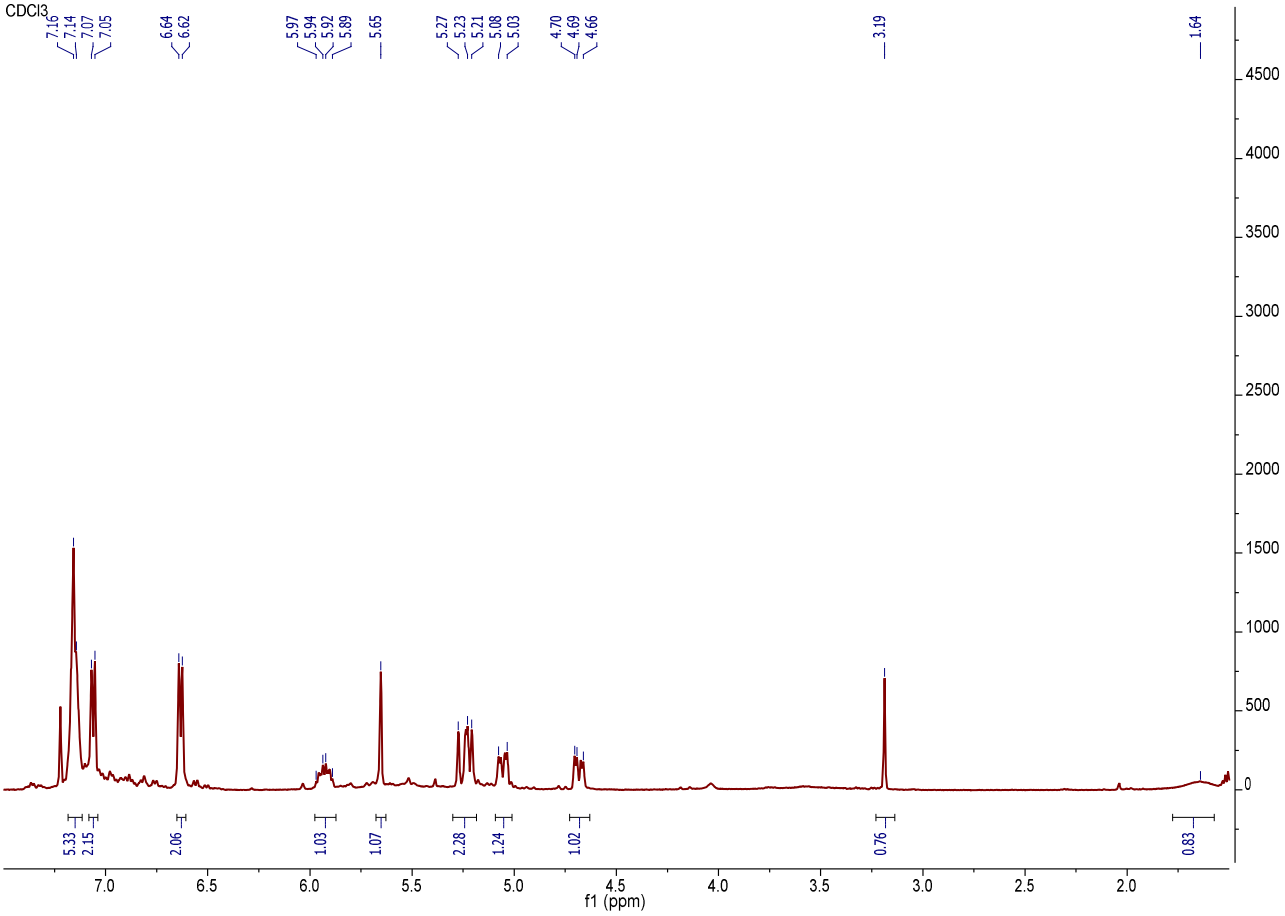

CDCl3
132.95
131.28
130.03
129.23
128.88
128.71
128.53
128.35
127.81
127.78
86.93
54.17
33.93
f1 (ppm)

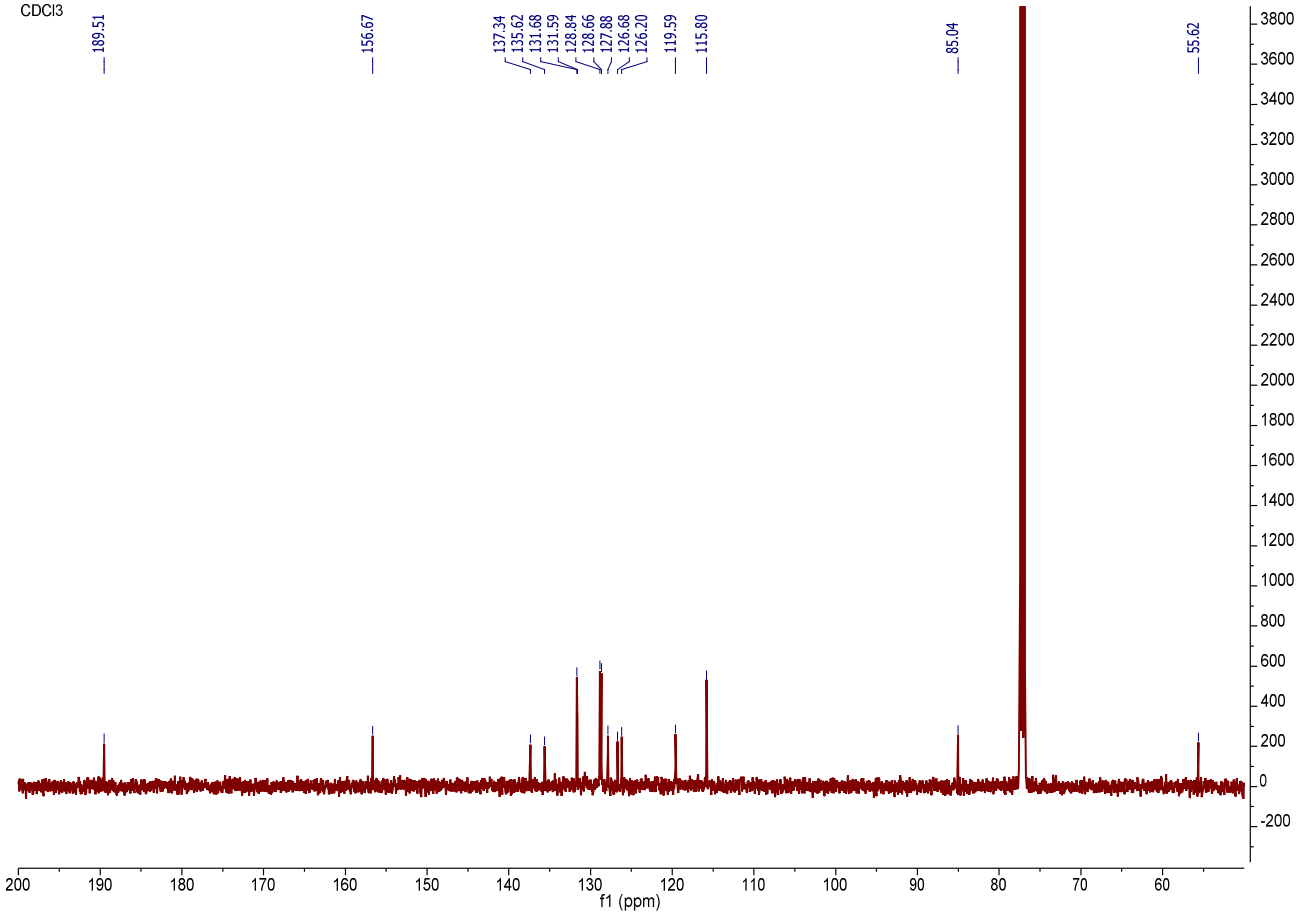

CDCl3
f2 (ppm)
f1 (ppm)

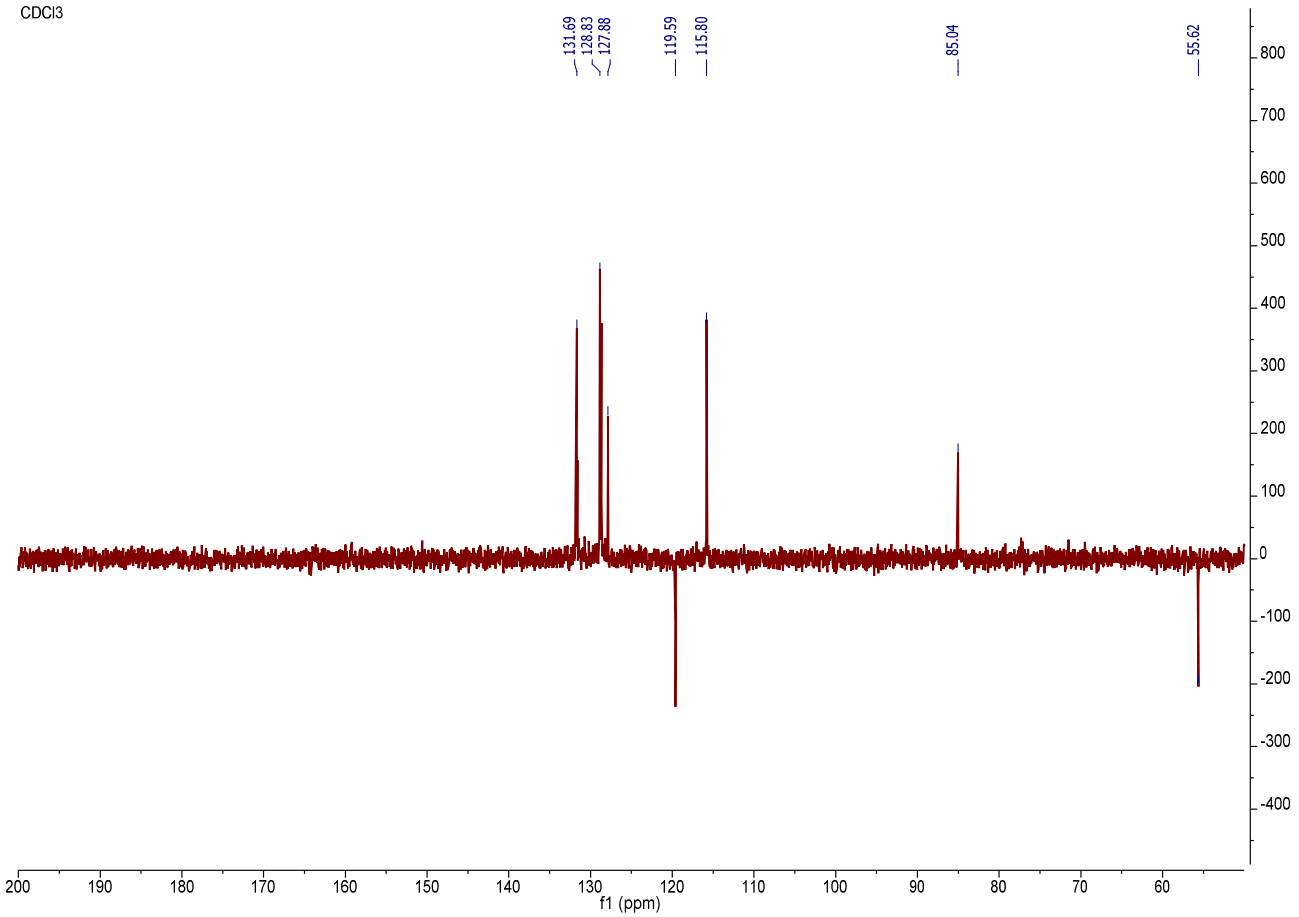

CDCl3
f2 (ppm)
f1 (ppm)

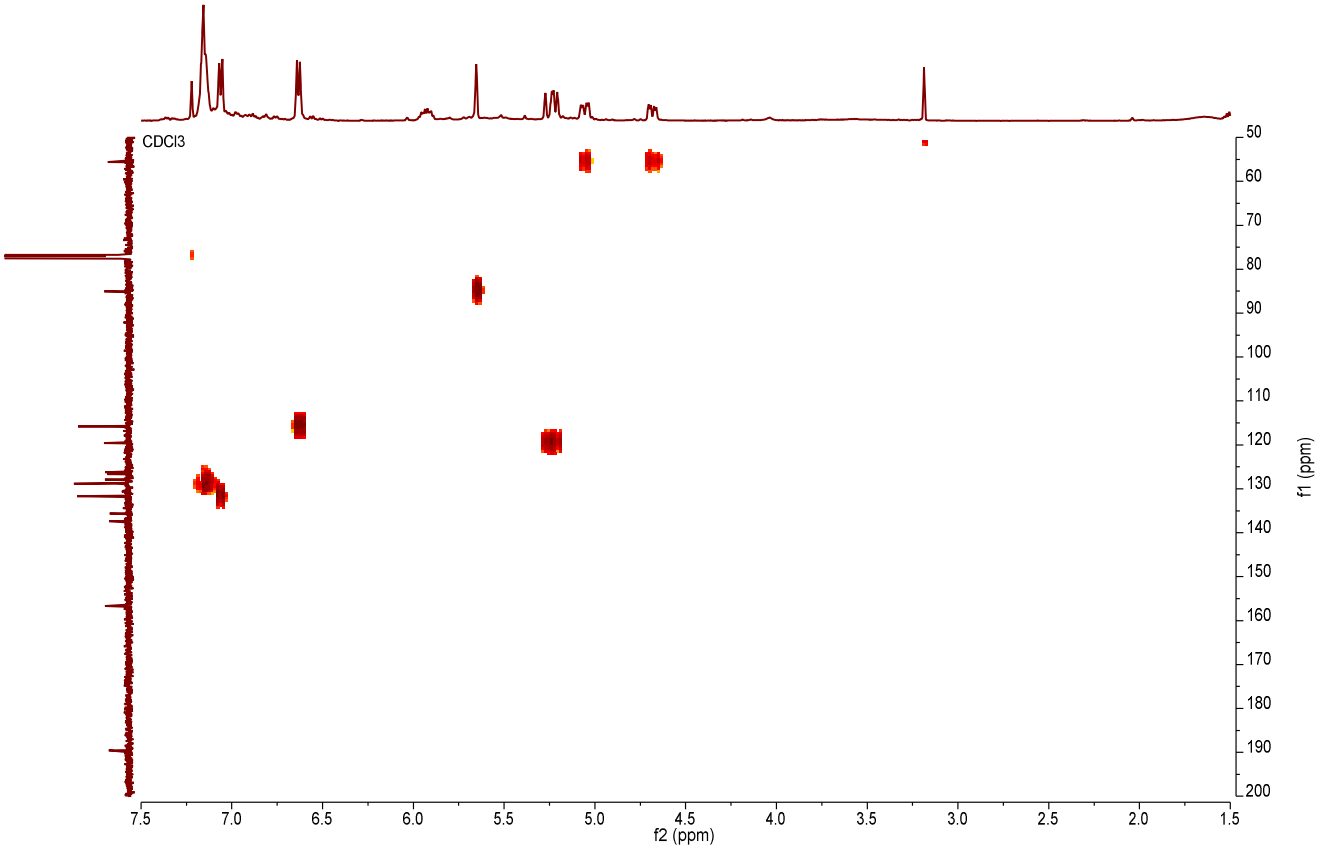

HO
N
S
S
HO

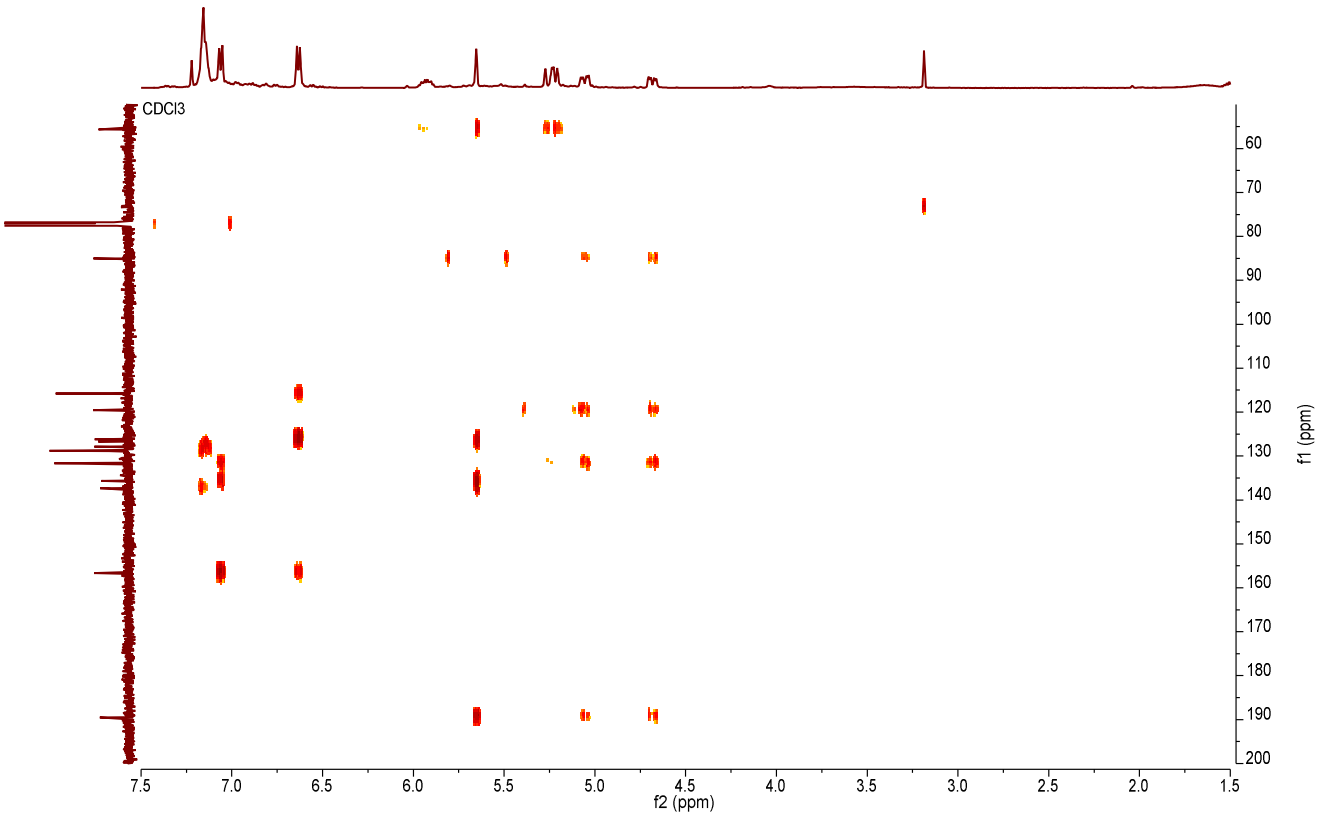
2k

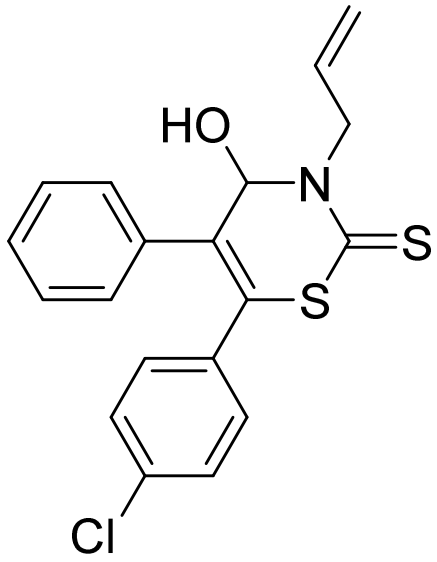

CDCl3
7.16
7.14
7.07
7.05
6.64
6.62
5.97
5.94
5.92
5.89
5.65
5.27
5.23
5.21
5.08
5.03
4.70
4.69
4.66
3.19
1.64
4500
4000
3500
3000
2500
2000
1500
1000
500
0
5.33
2.15
2.06
1.03
1.07
2.28
1.24
1.02
0.76
0.83
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
f1 (ppm)


CDCl3
189.51
156.67
137.34
135.62
131.68
131.59
128.84
128.66
127.88
126.68
126.20
119.59
115.80
85.04
55.62
f1 (ppm)

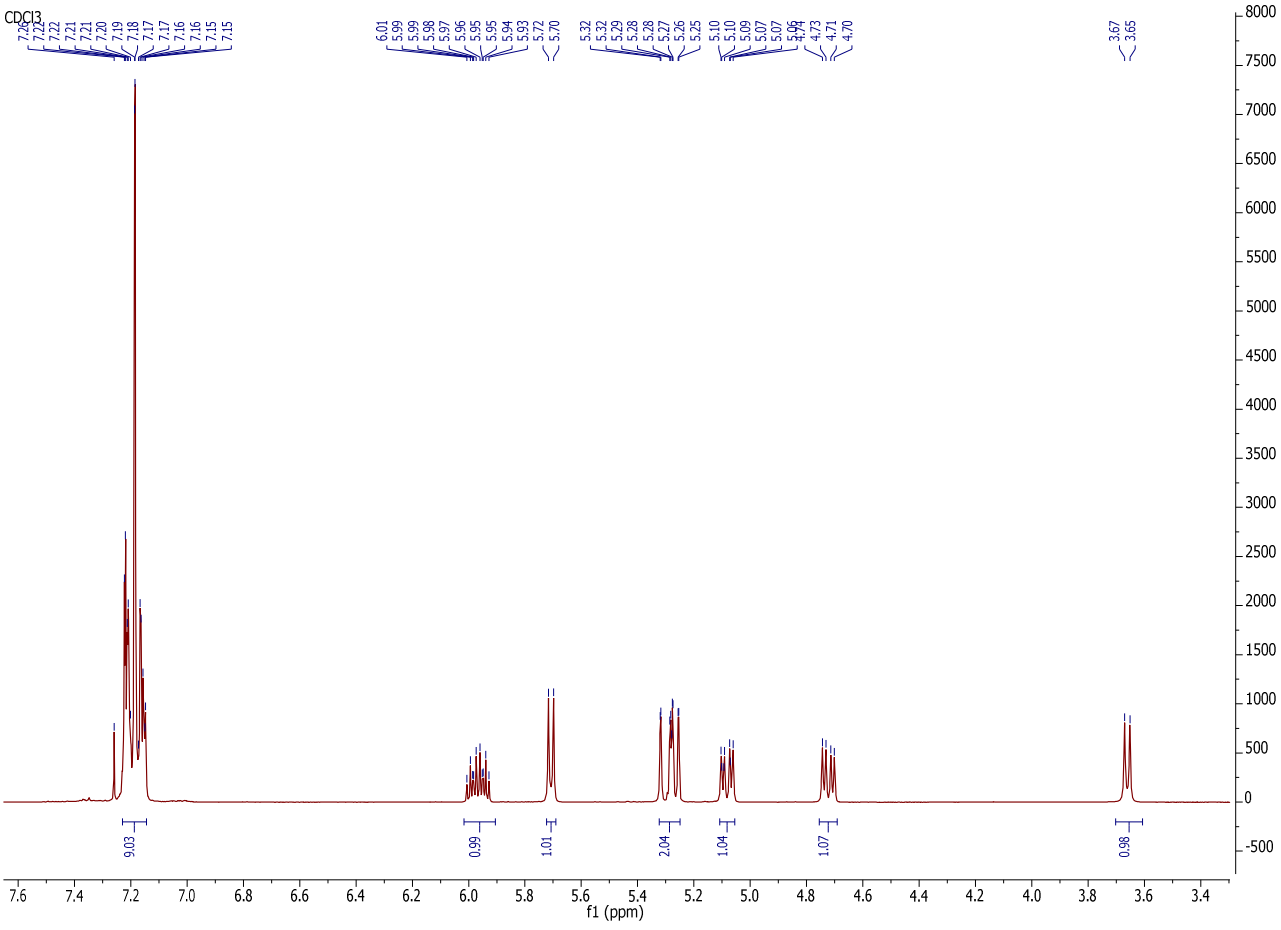

CDCl3
131.69
128.83
127.88
119.59
115.80
85.04
55.62
f1 (ppm)

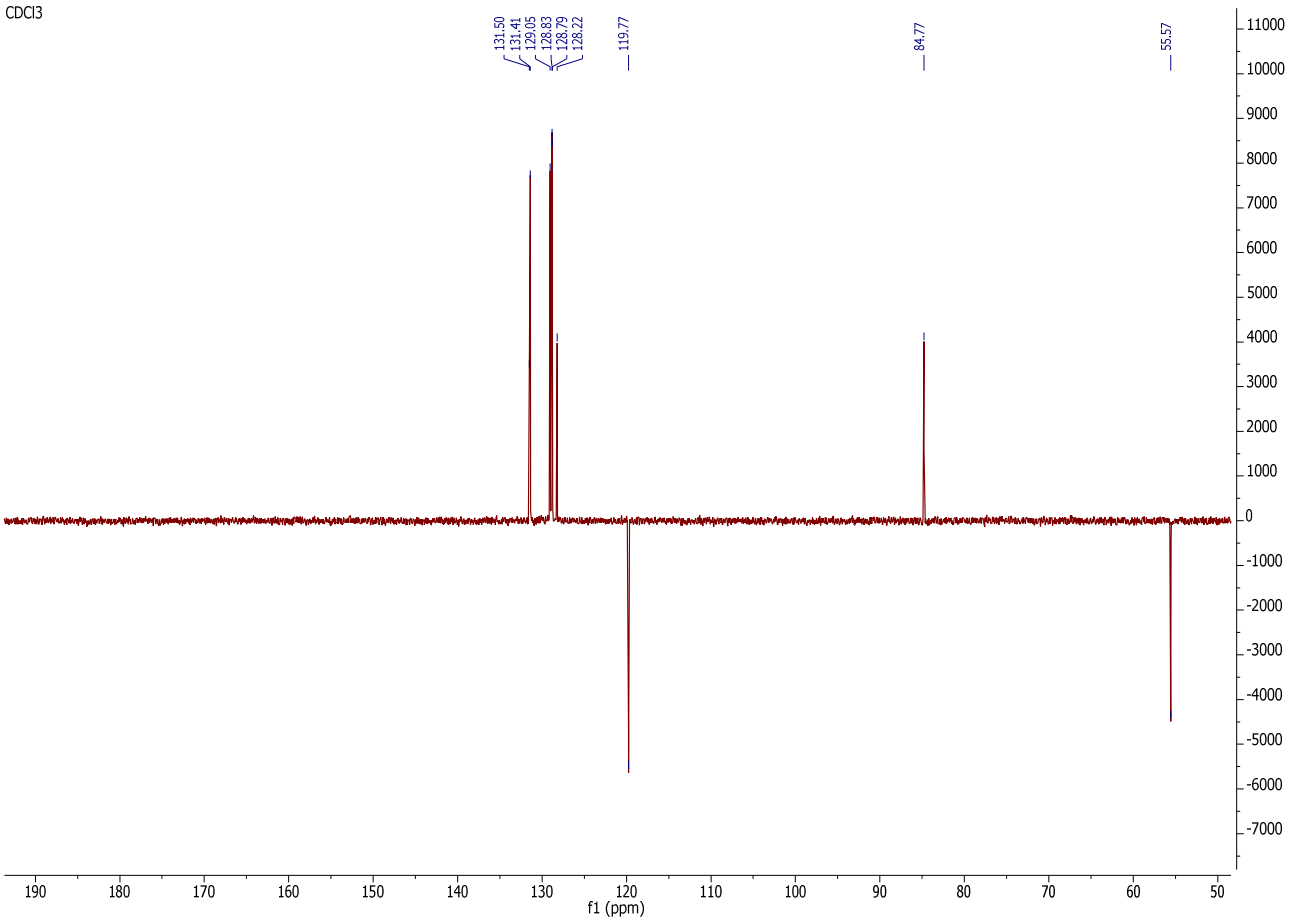

CDCl3
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
f1 (ppm)
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f2 (ppm)

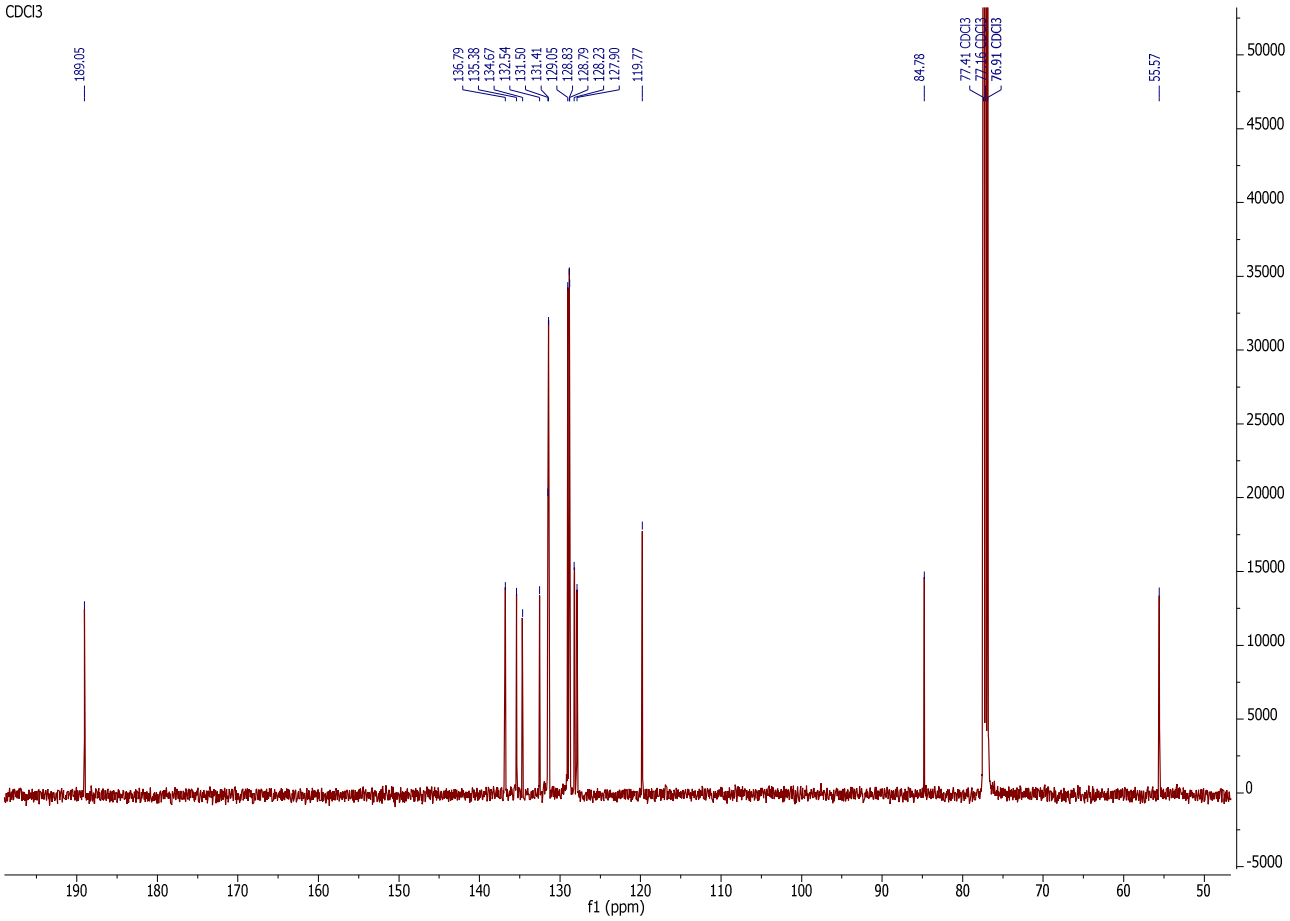

CDCl3
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
f1 (ppm)
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f2 (ppm)

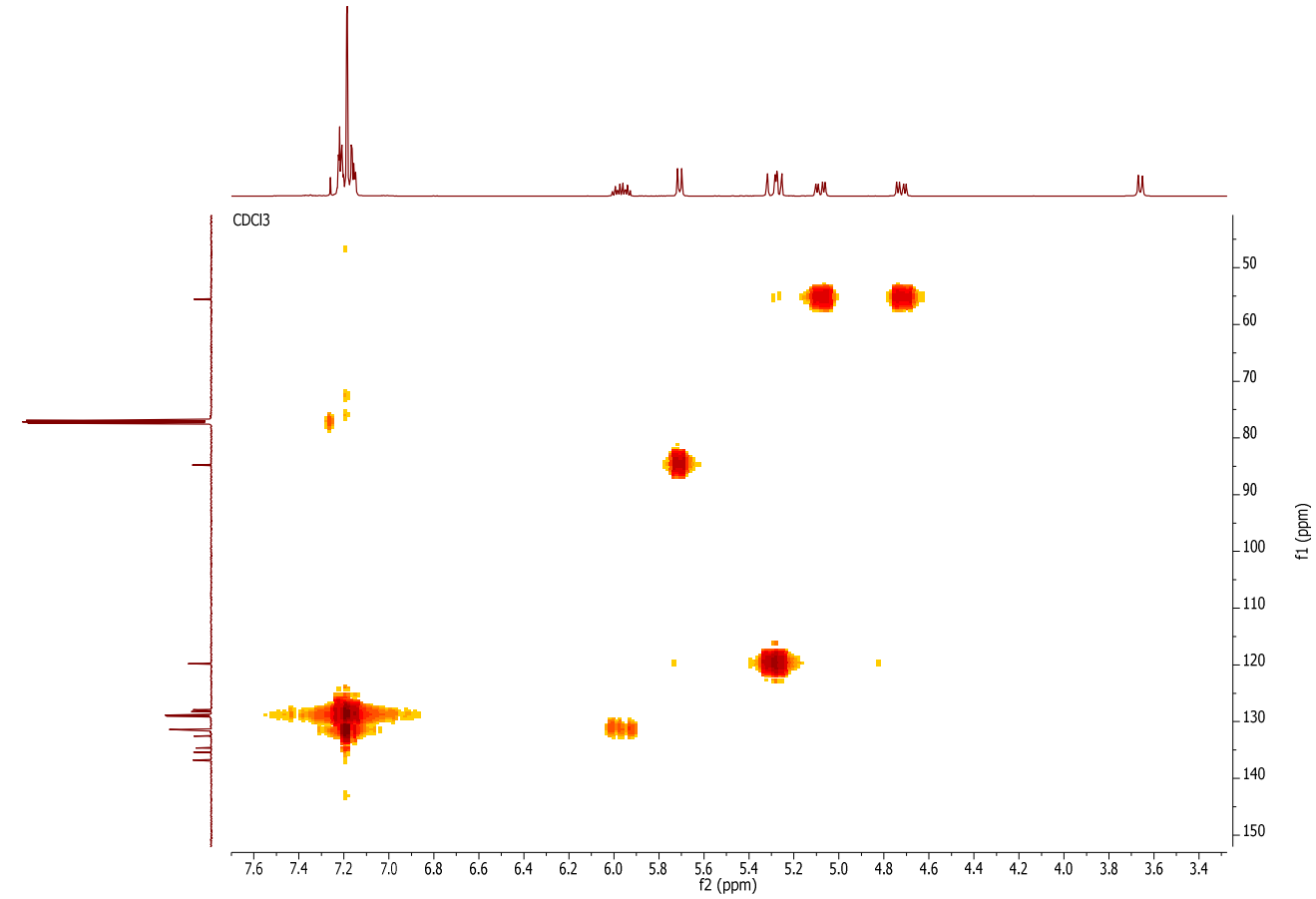


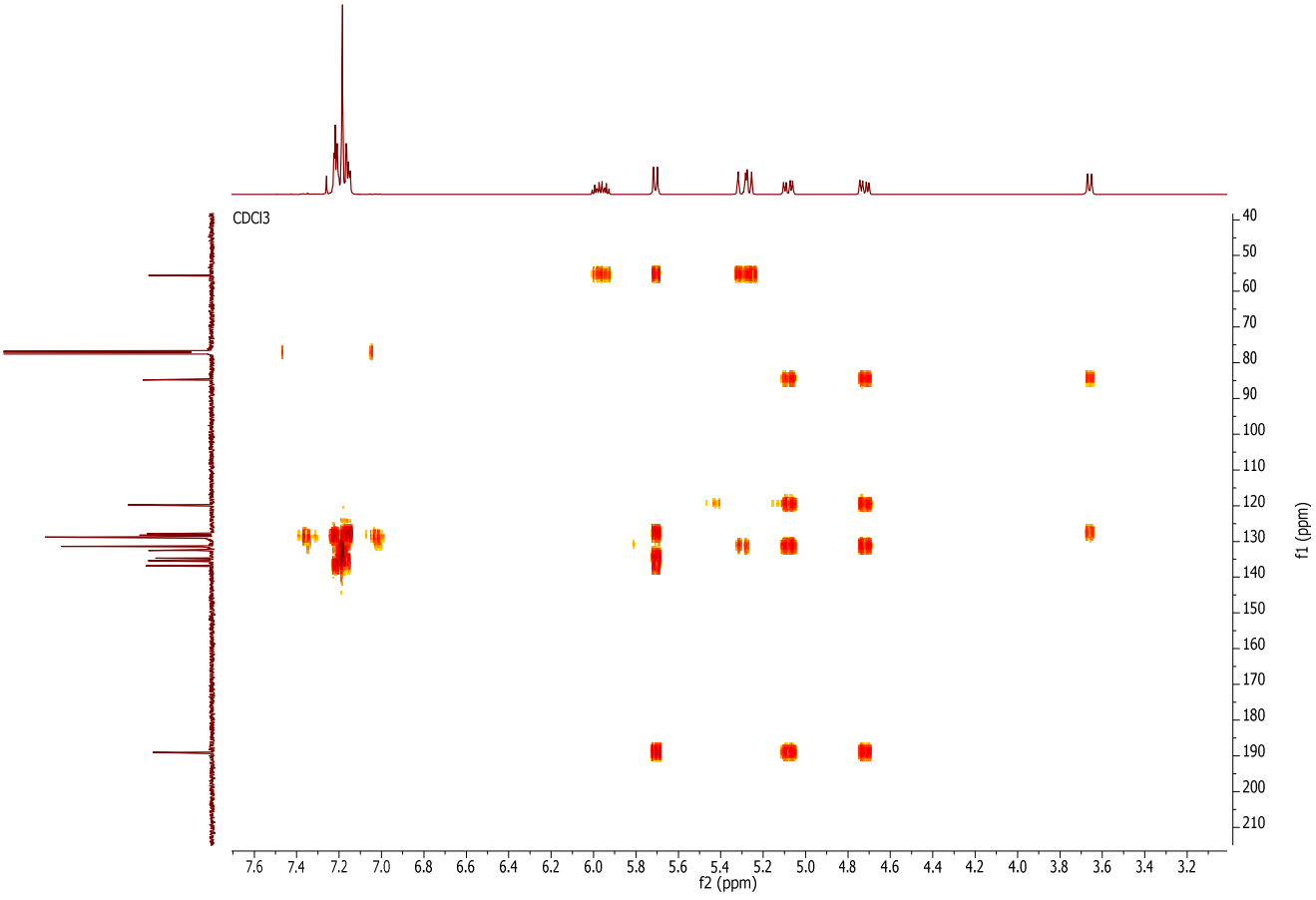
2l

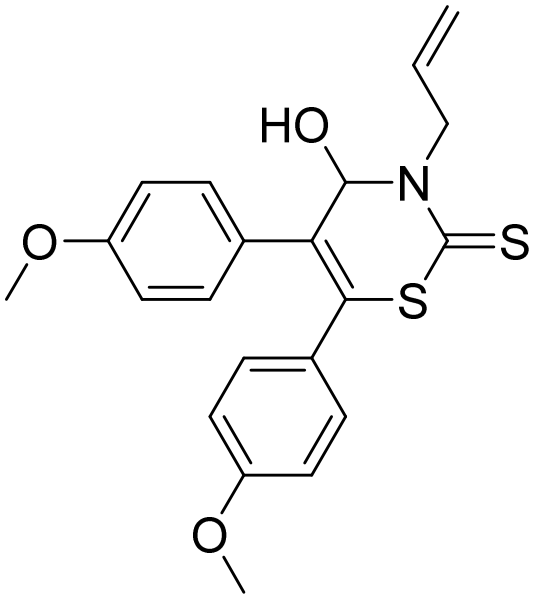



CDCl3
131.50
131.41
129.05
128.83
128.79
128.22
119.77
84.77
55.57
f1 (ppm)

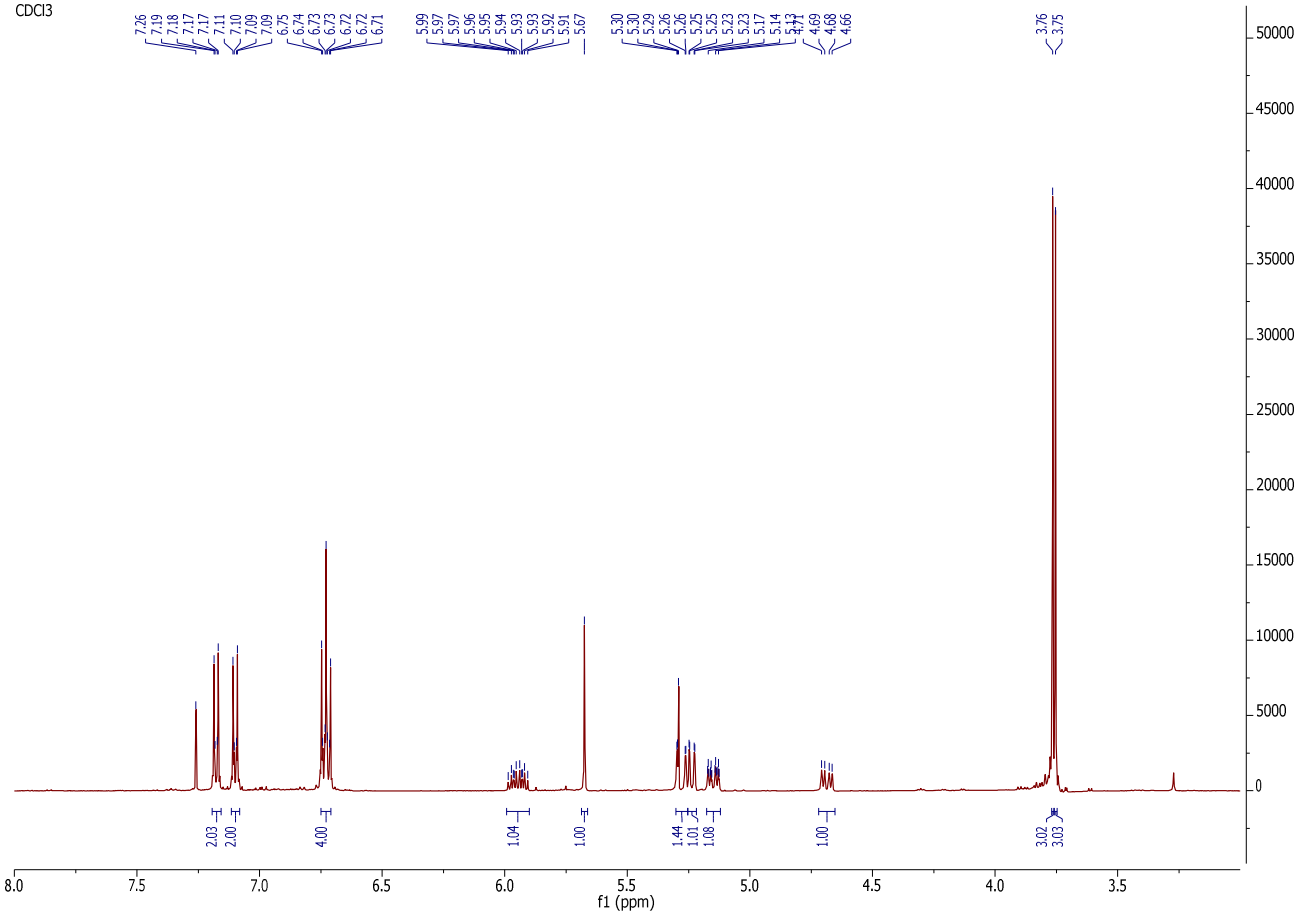

CDCl3
189.05
136.79
135.38
134.67
132.54
131.50
131.41
129.05
128.83
128.79
128.23
127.90
119.77
84.78
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
55.57
f1 (ppm)

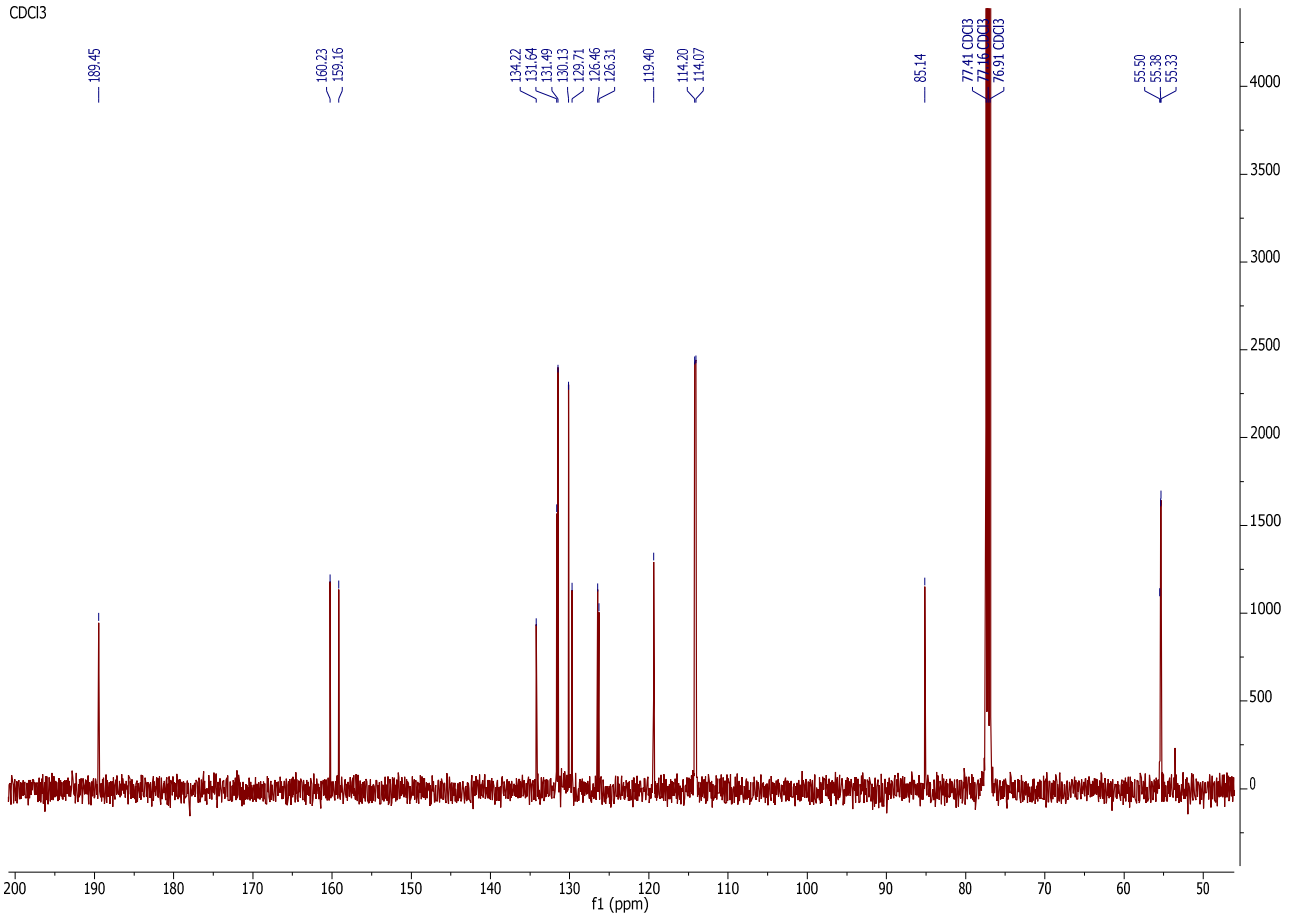

CDCl3
f1 (ppm)
f2 (ppm)

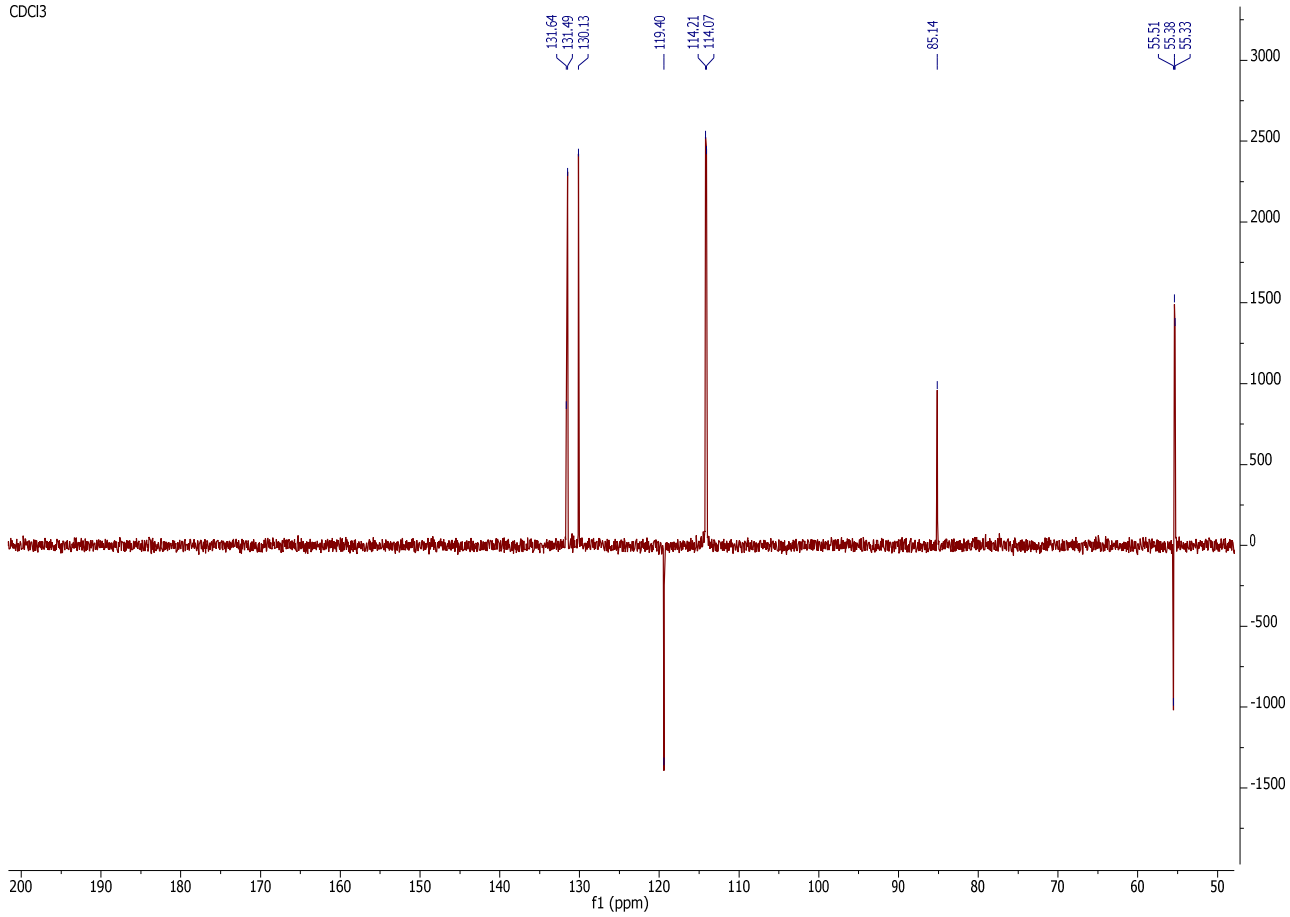

CDCl3
f1 (ppm)
f2 (ppm)

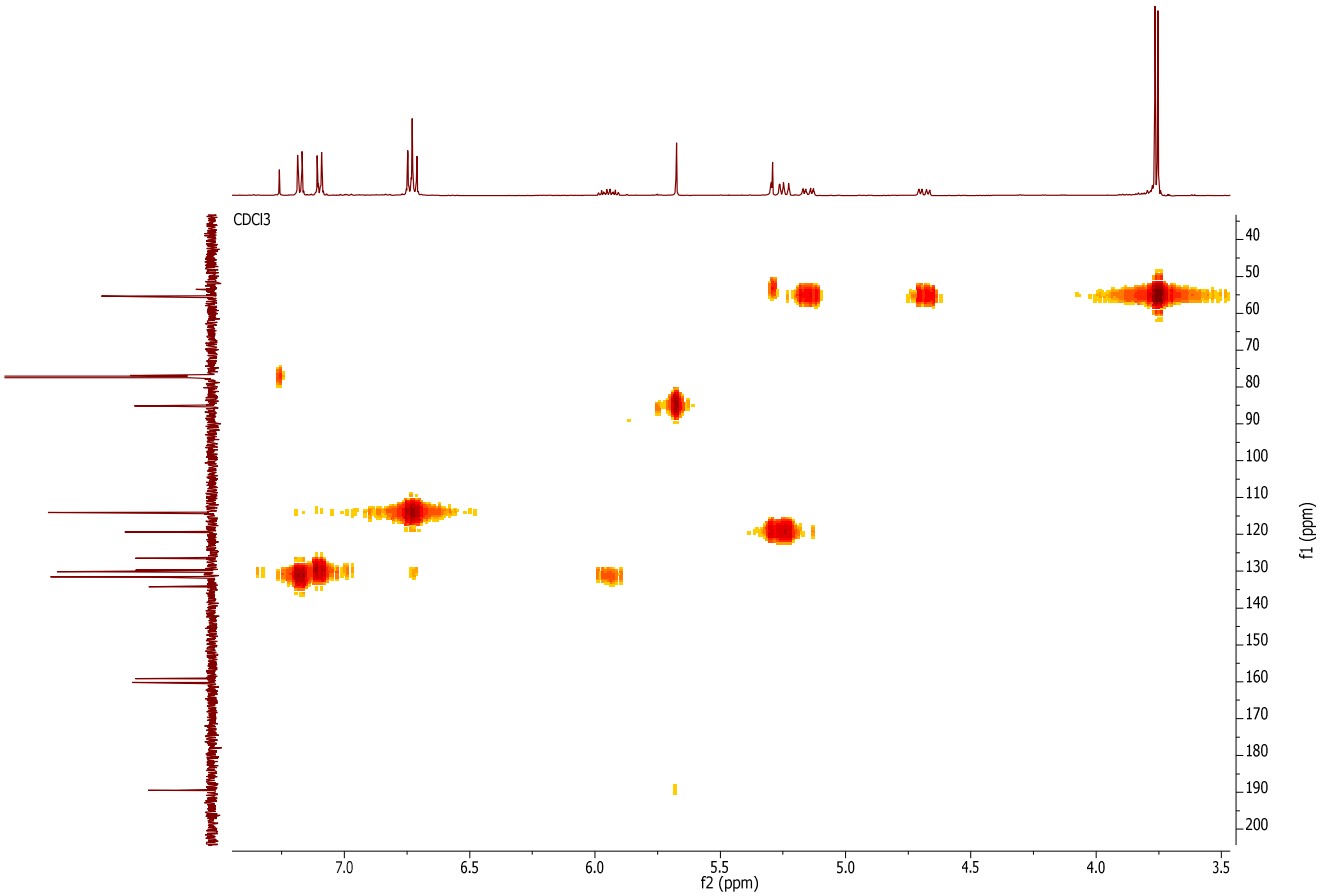


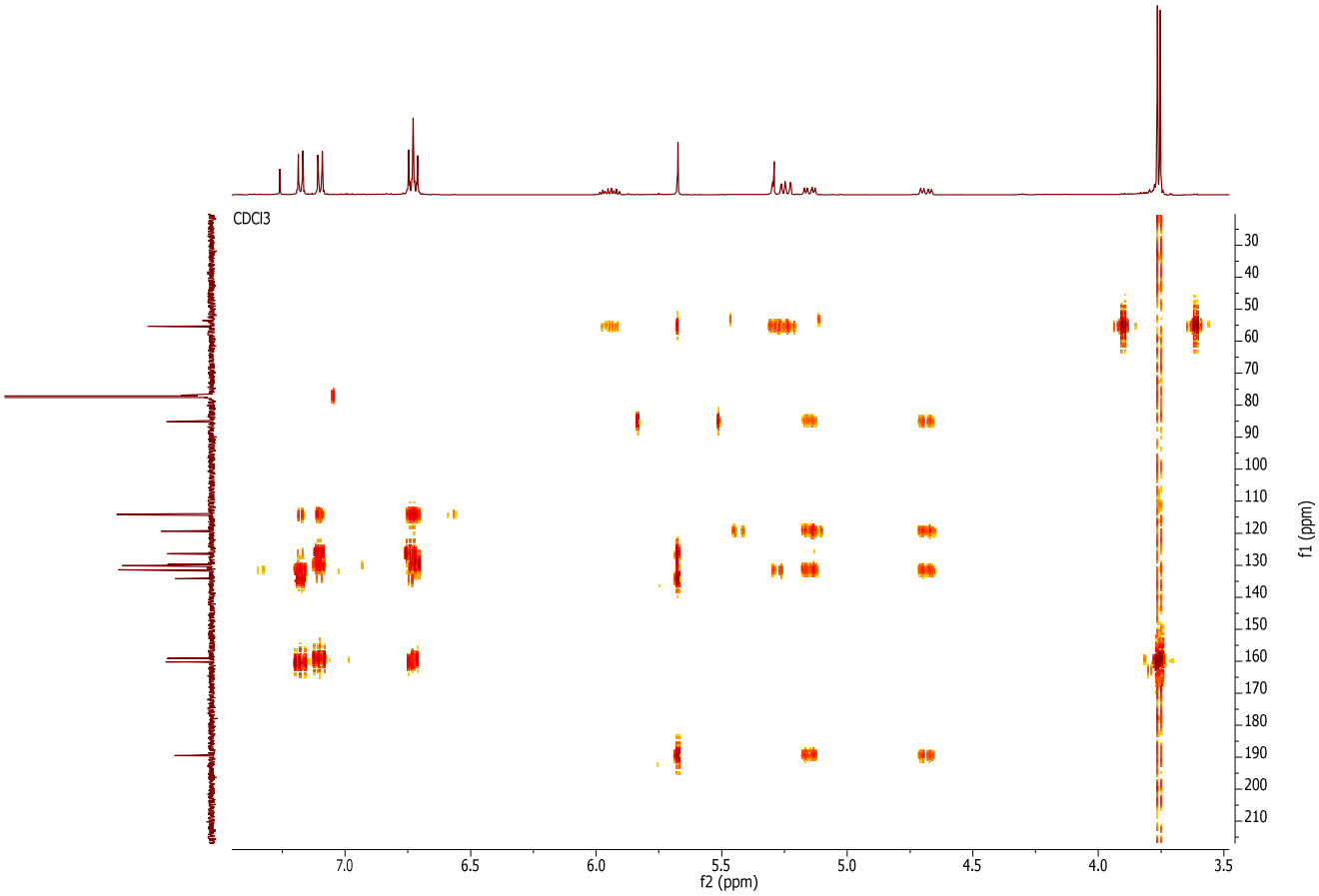
2m

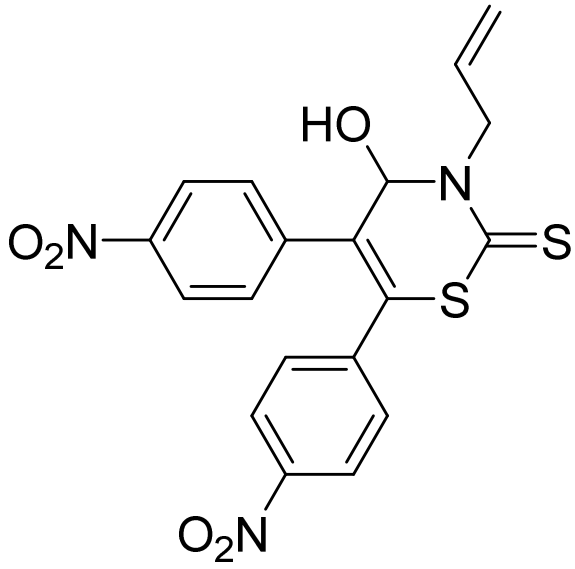



CDCl3
189.45
160.23
159.16
134.22
131.64
131.49
130.13
129.71
126.46
126.31
119.40
114.20
114.07
85.14
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
55.50
55.38
55.33
f1 (ppm)

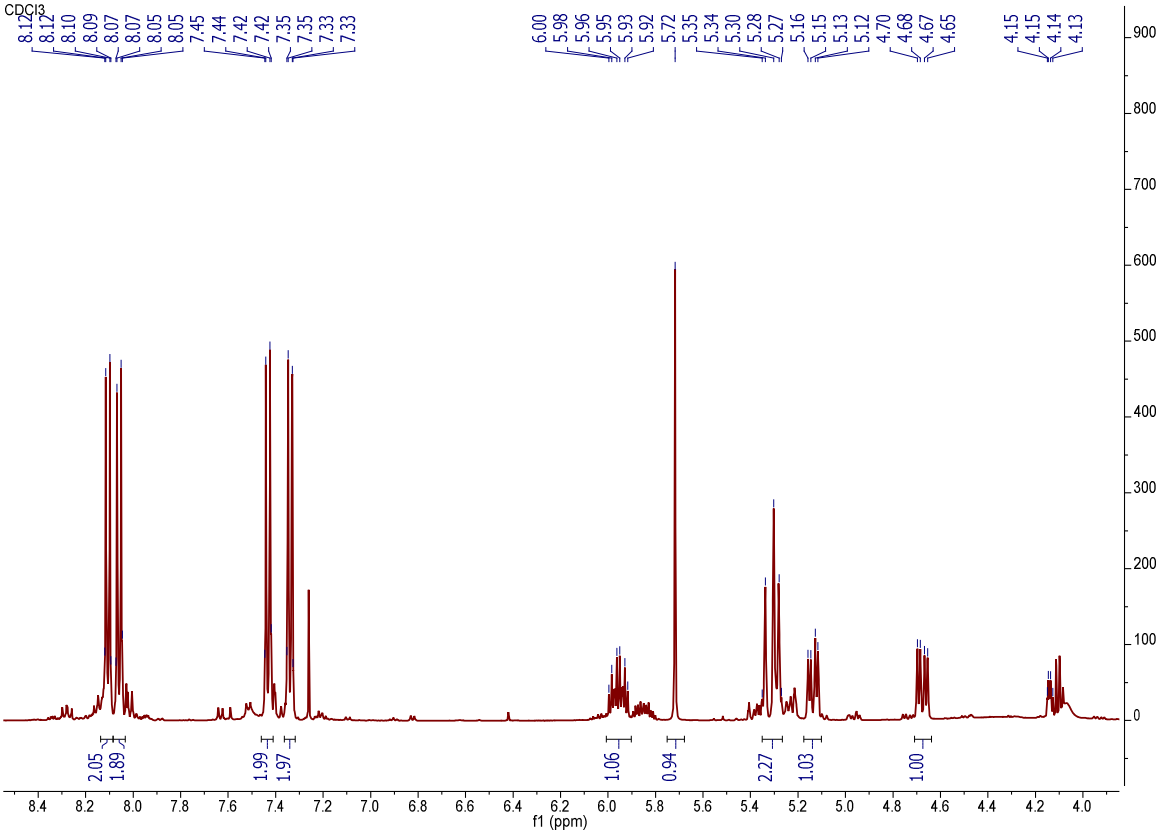

CDCl3
131.64
131.49
130.13
119.40
114.21
114.07
85.14
55.51
55.38
55.33
f1 (ppm)

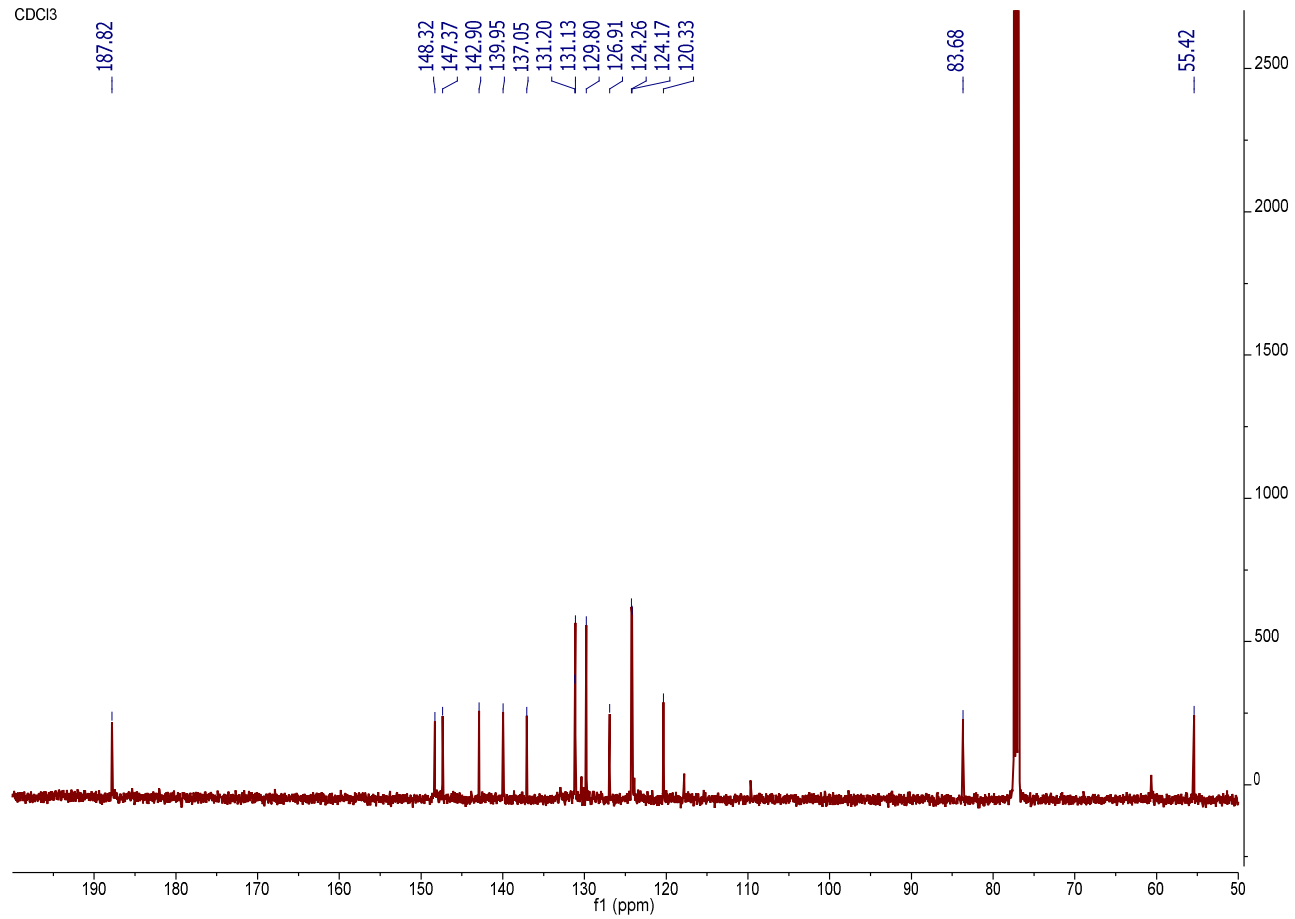

CDCl3
f2 (ppm)
f1 (ppm)

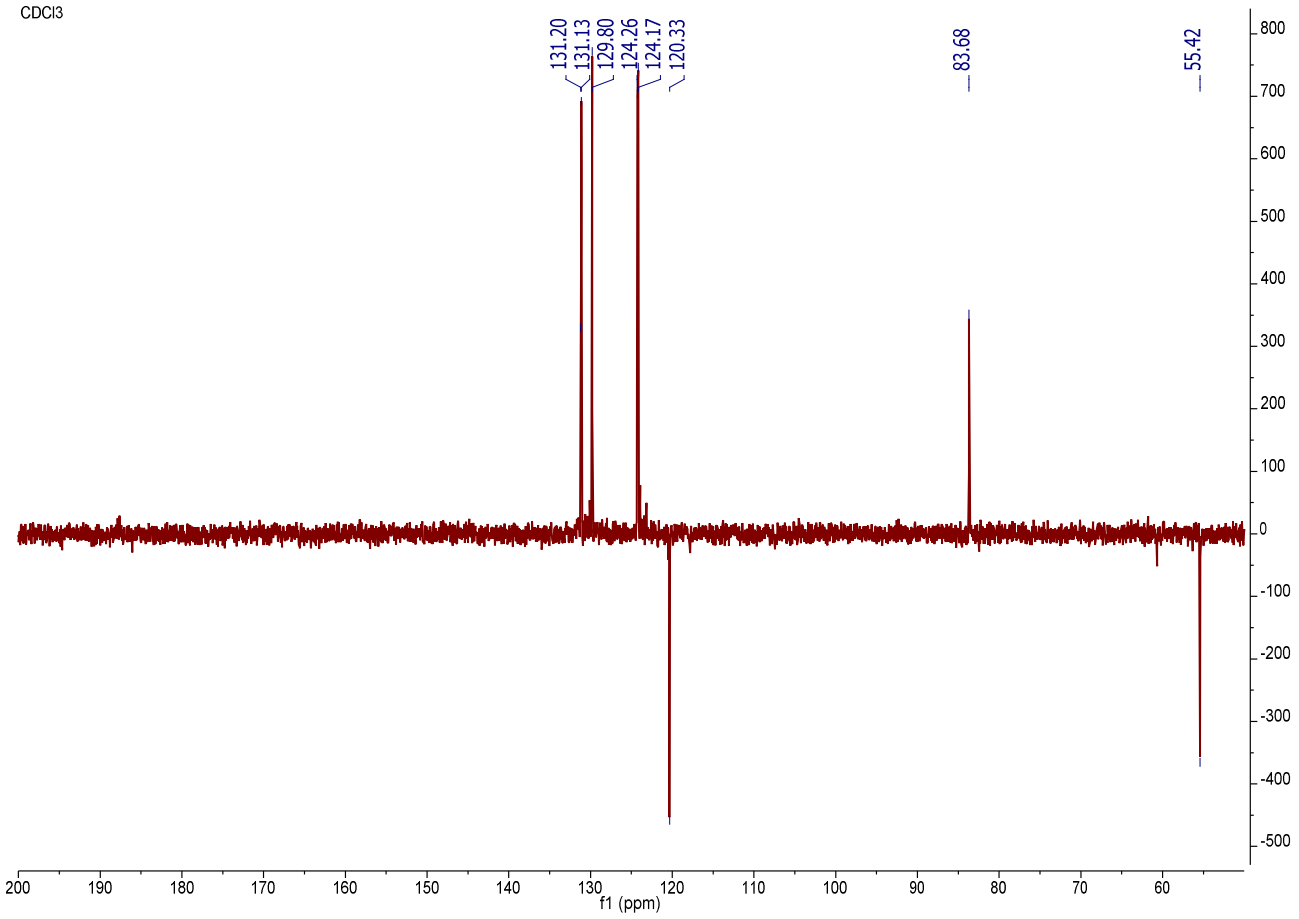

CDCl3
f2 (ppm)
f1 (ppm)

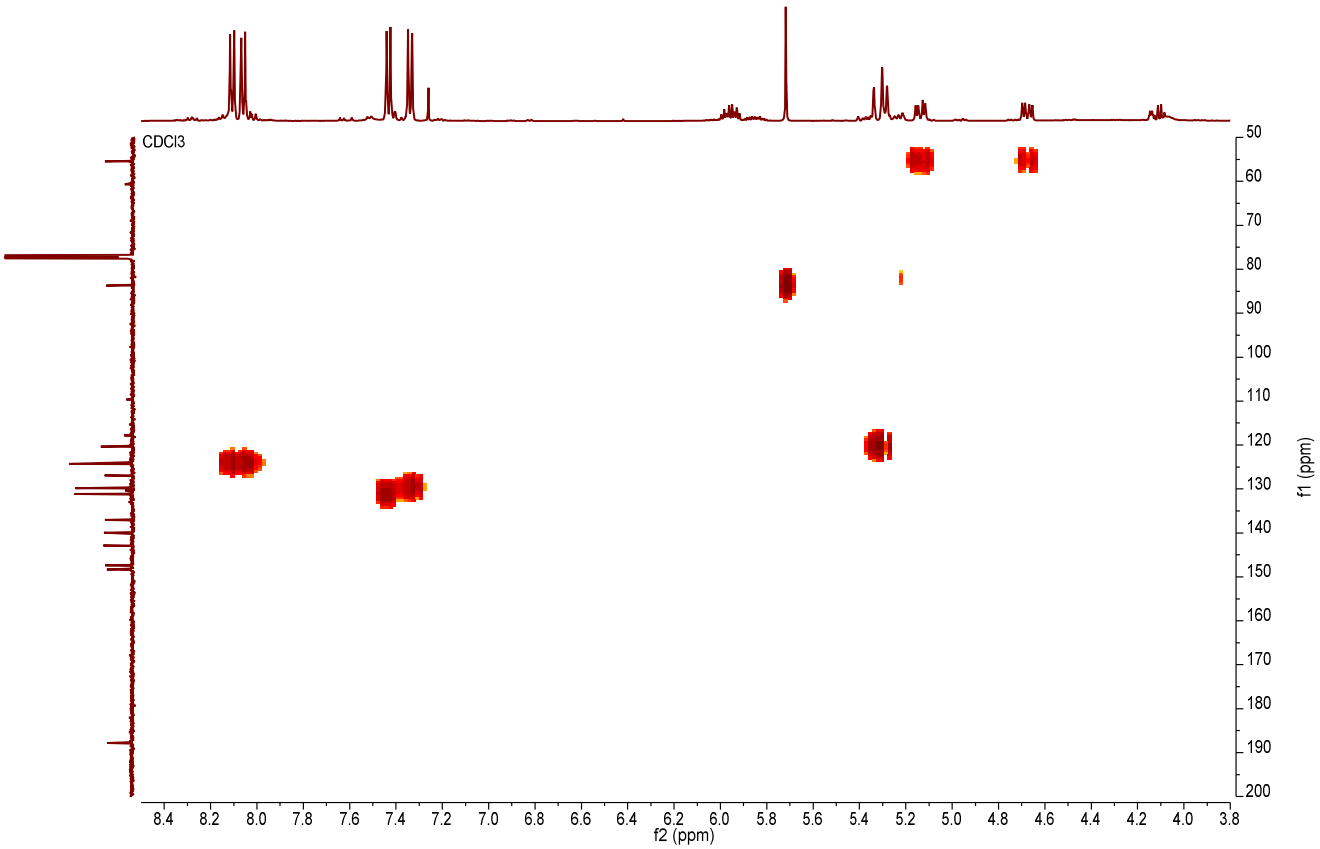

HO
N
S
S
O_2N
O_2N

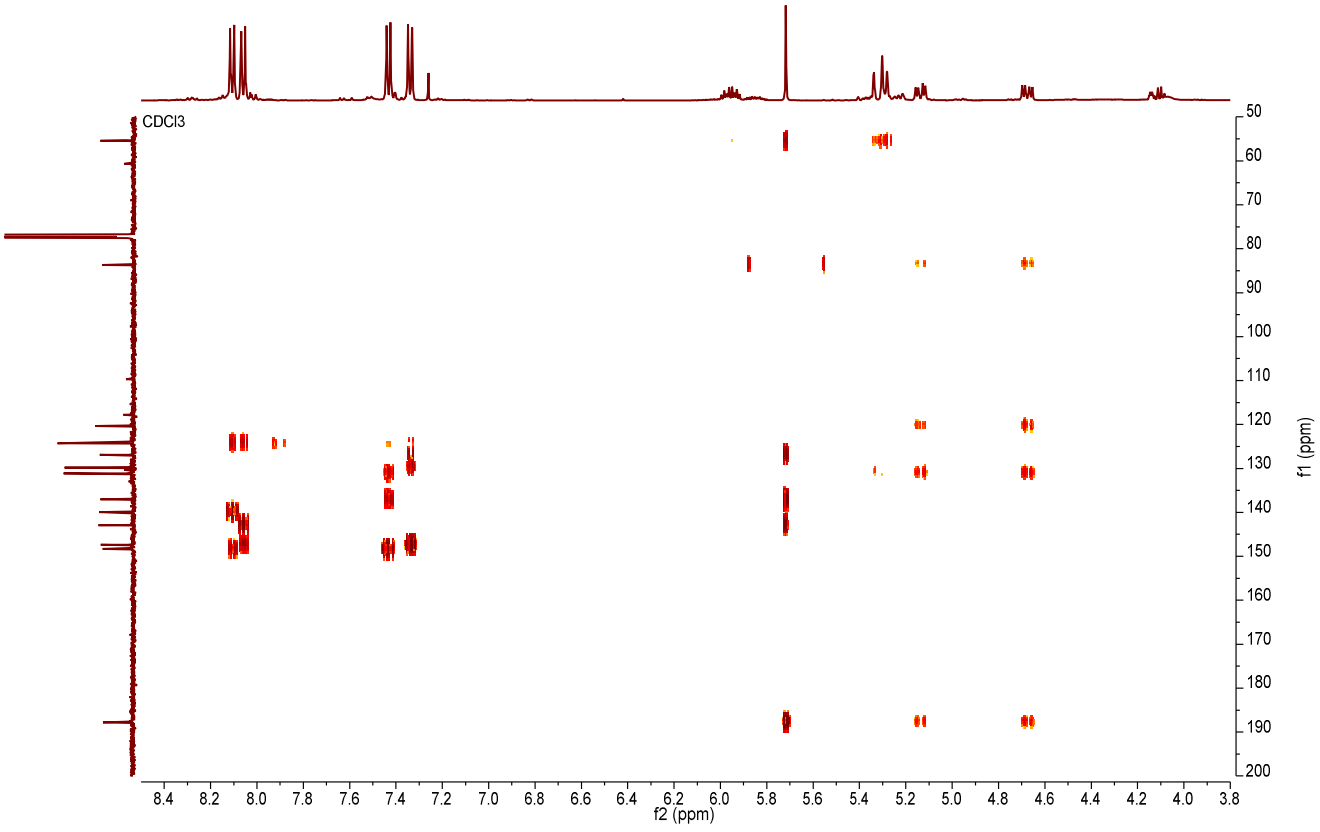
2n

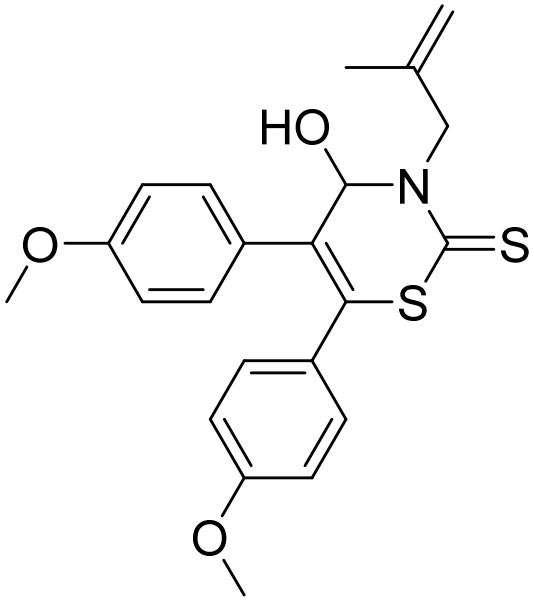

CDCl3
8.12
8.12
8.10
8.09
8.07
8.07
8.05
8.05
7.45
7.44
7.42
7.42
7.35
7.35
7.33
7.33
6.00
5.98
5.96
5.95
5.93
5.92
5.72
5.35
5.34
5.30
5.28
5.27
5.16
5.15
5.13
5.12
4.70
4.68
4.67
4.65
4.15
4.15
4.14
4.13
2.05
1.89
1.99
1.97
1.06
0.94
2.27
1.03
1.00
f1 (ppm)


CDCl3
187.82
148.32
147.37
142.90
139.95
137.05
131.20
131.13
129.80
126.91
124.26
124.17
120.33
83.68
55.42
f1 (ppm)

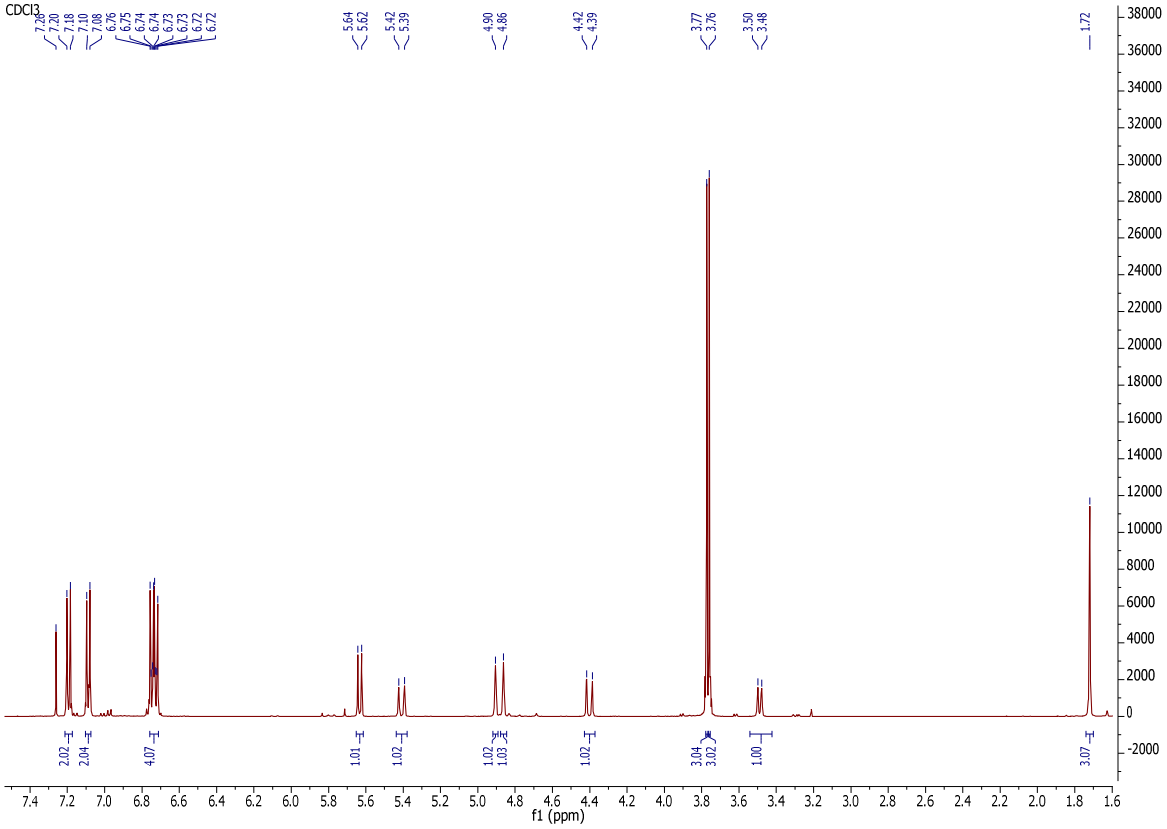

CDCl3
131.20
131.13
129.80
124.26
124.17
120.33
83.68
55.42
f1 (ppm)

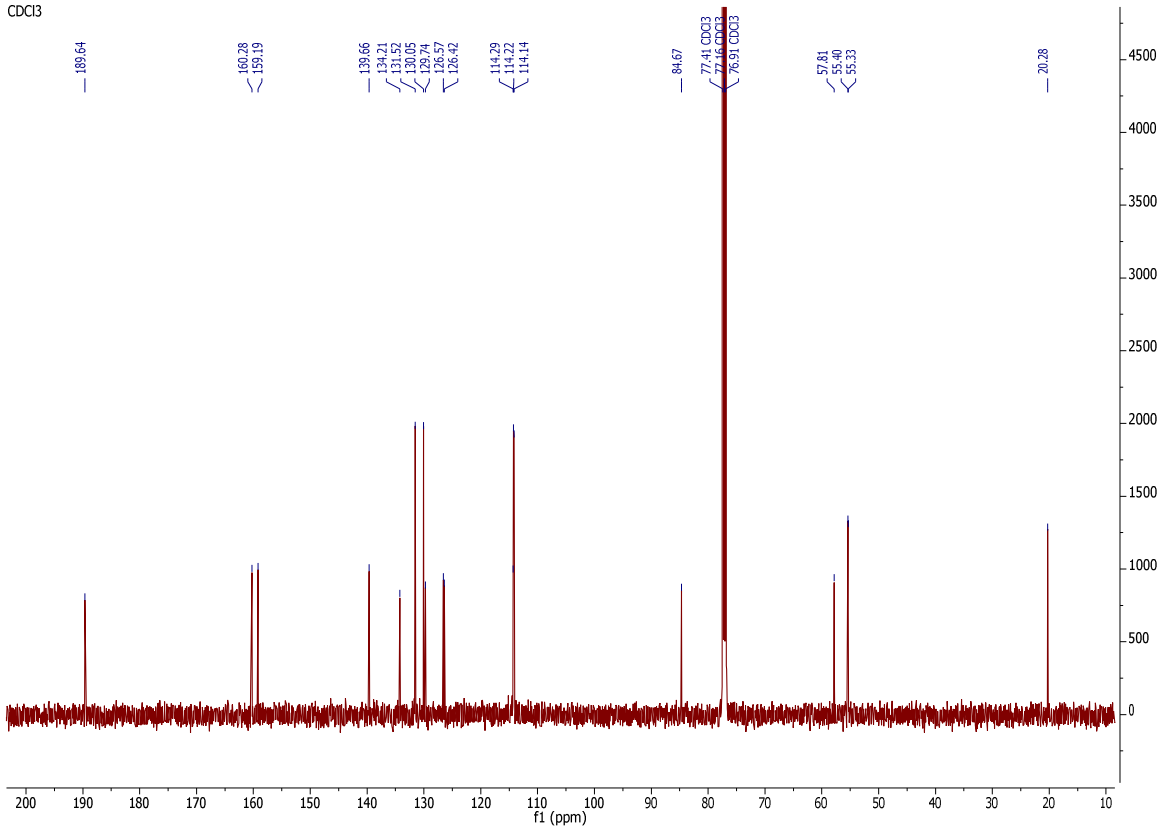

CDCl3
f2 (ppm)
f1 (ppm)

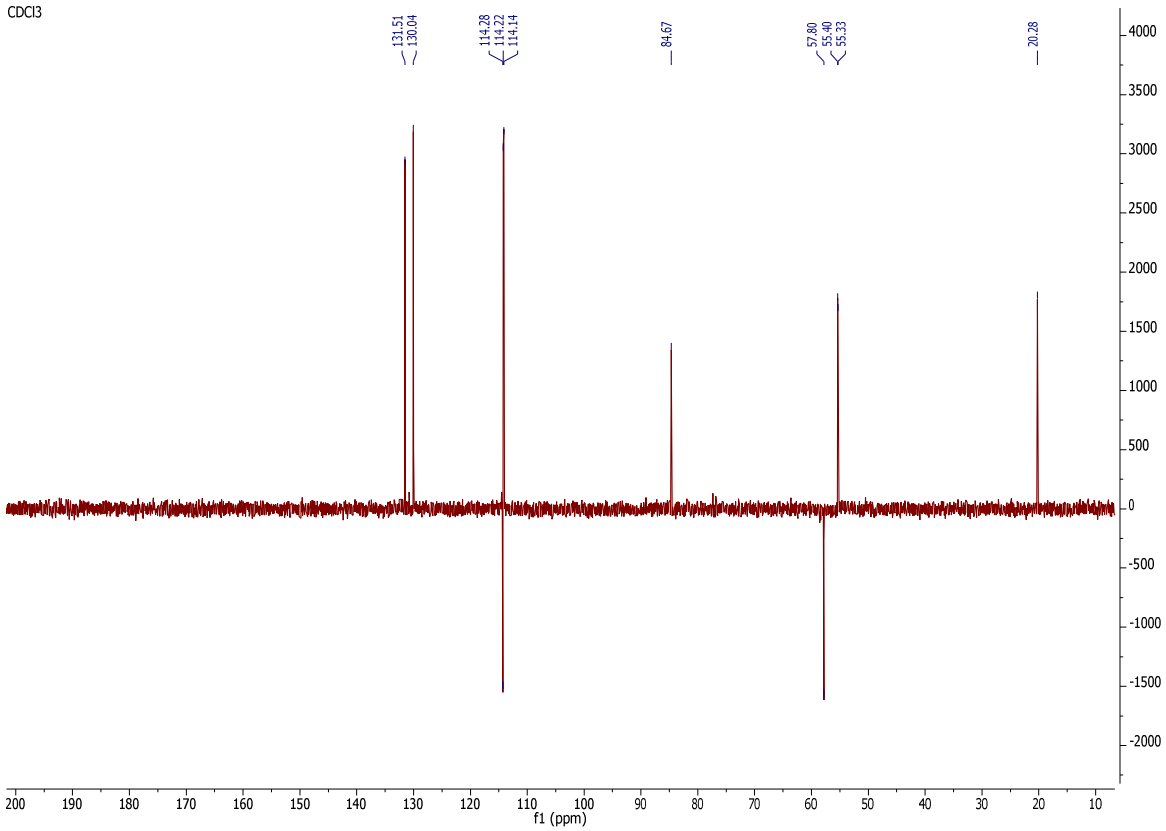

CDCl3
f2 (ppm)
f1 (ppm)

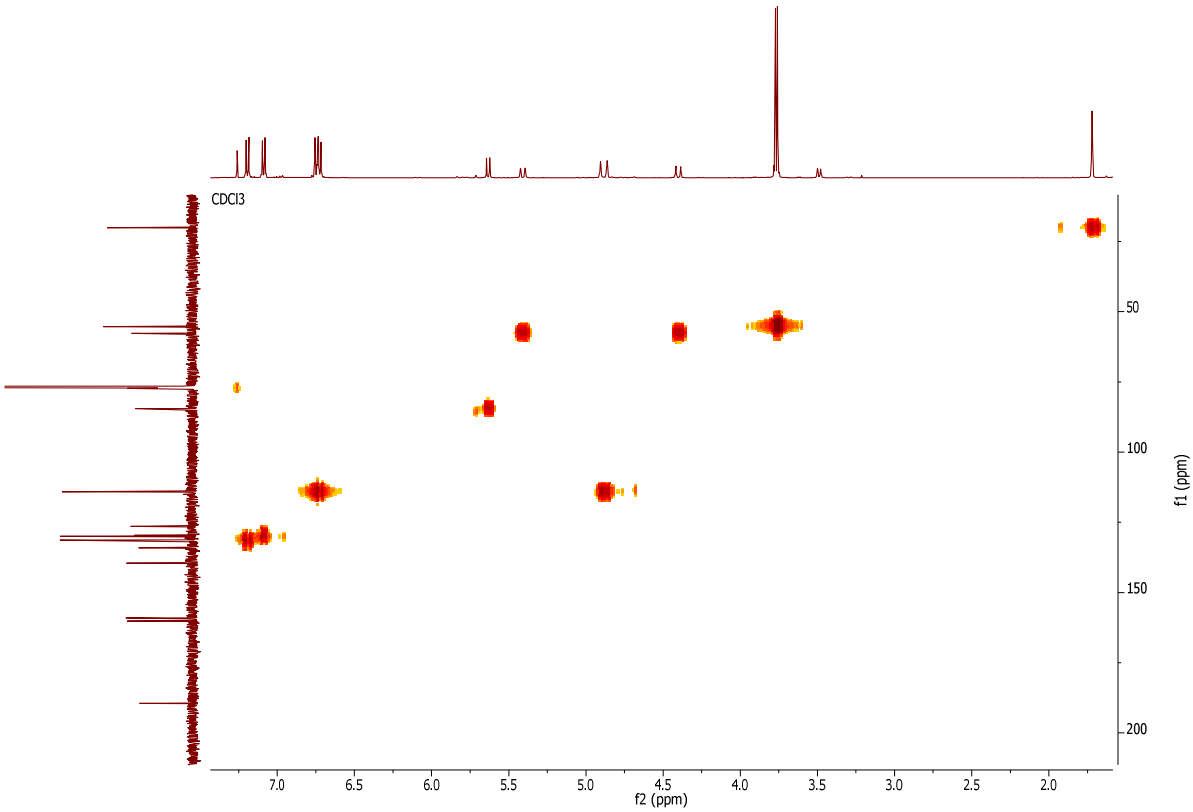

HO
N
S
O
S
O

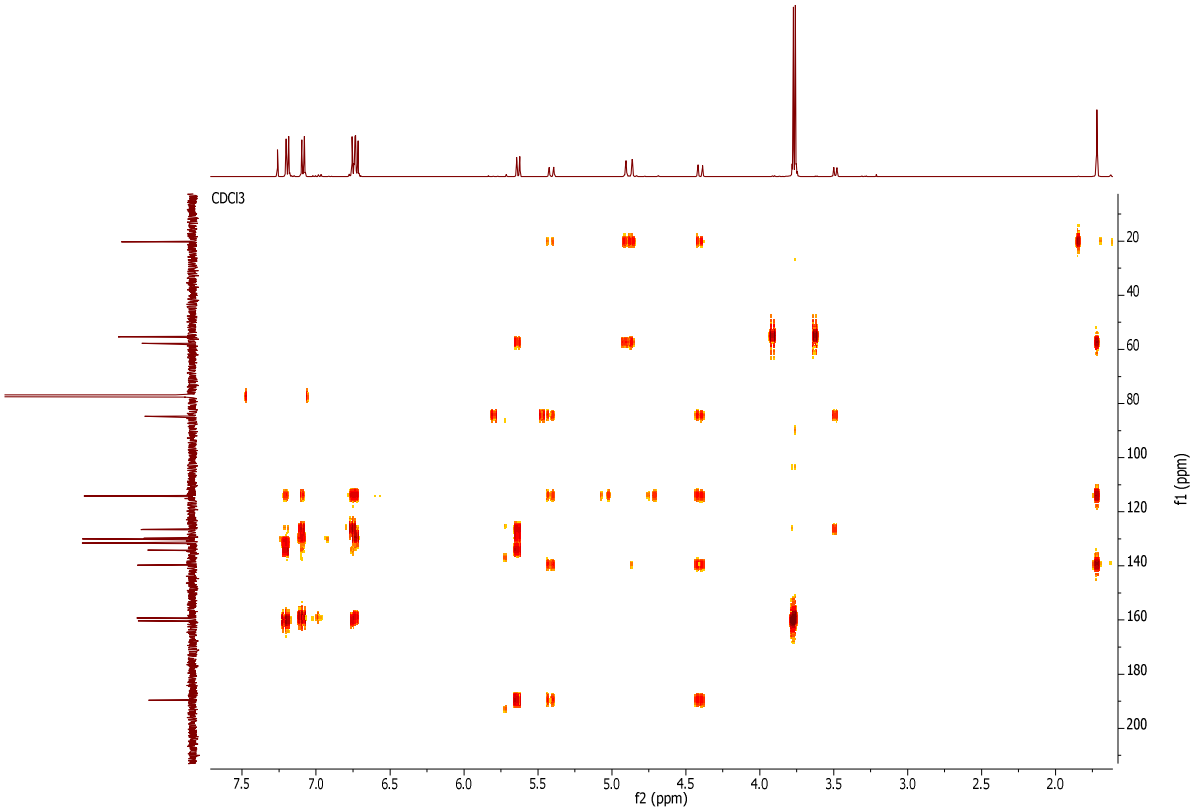
2o

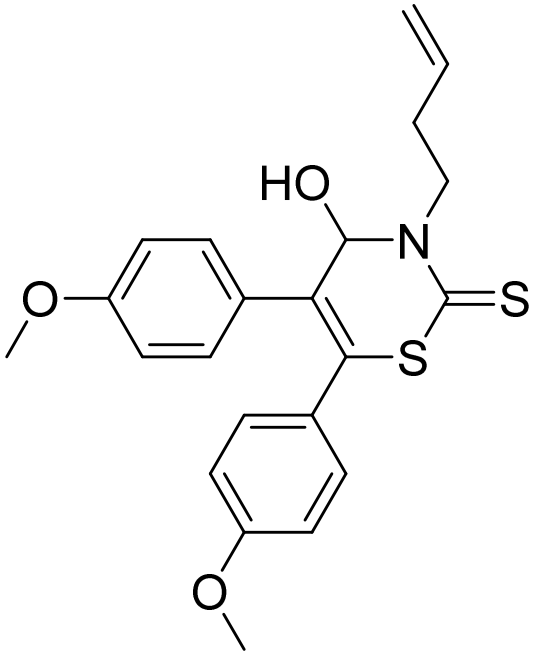

CDCl3
7.26
7.20
7.18
7.10
7.08
6.76
6.75
6.74
6.74
6.73
6.73
6.72
6.72
5.64
5.62
5.42
5.39
4.90
4.86
4.42
4.39
3.77
3.76
3.50
3.48
1.72
2.02
2.04
4.07
1.01
1.02
1.02
1.03
1.02
3.04
3.02
1.00
3.07
f1 (ppm)


CDCl3
189.64
160.28
159.19
139.66
134.21
131.52
130.05
129.74
126.57
126.42
114.29
114.22
114.14
84.67
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
57.81
55.40
55.33
20.28
f1 (ppm)

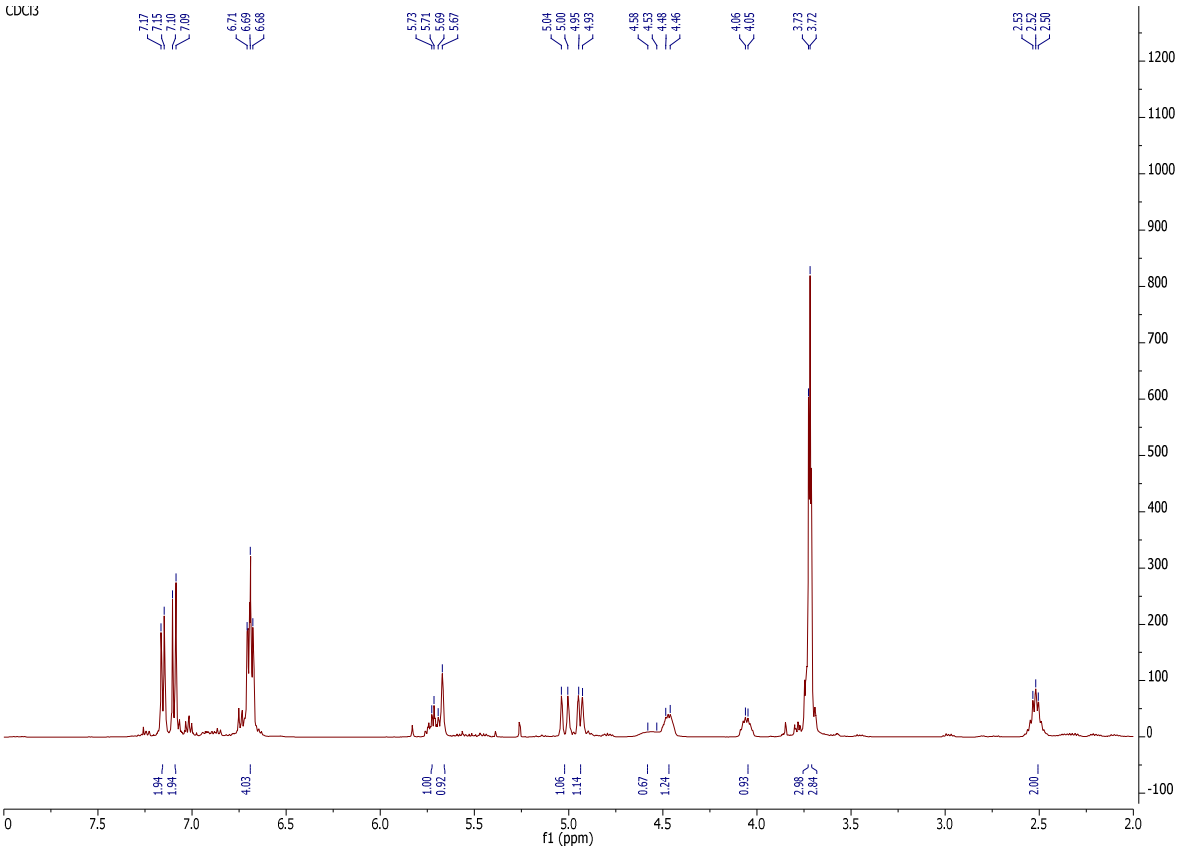

CDCl3
131.51
130.04
114.28
114.22
114.14
84.67
57.80
55.40
55.33
20.28
f1 (ppm)

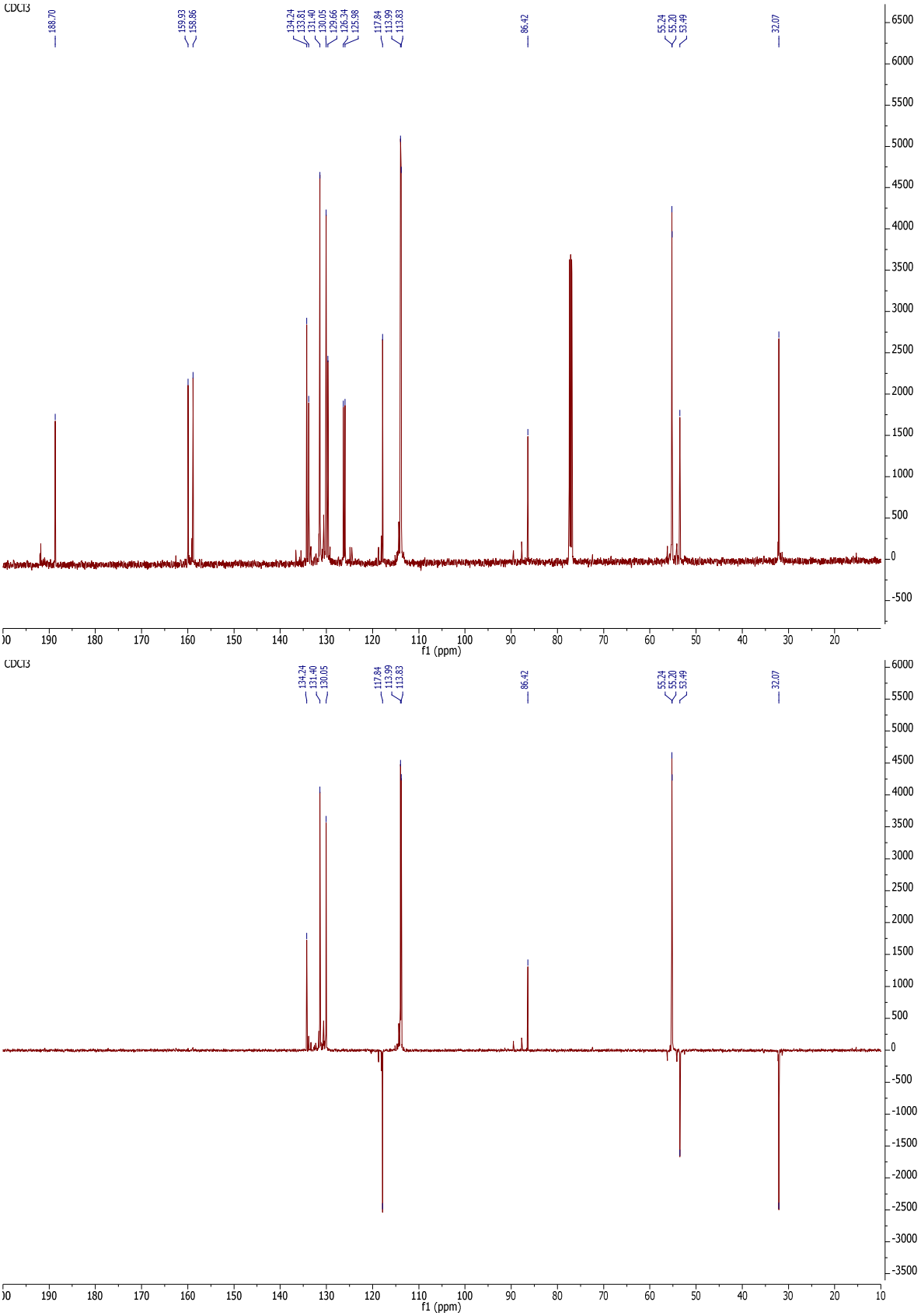

CDCl3
50
100
150
200
f1 (ppm)
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
f2 (ppm)

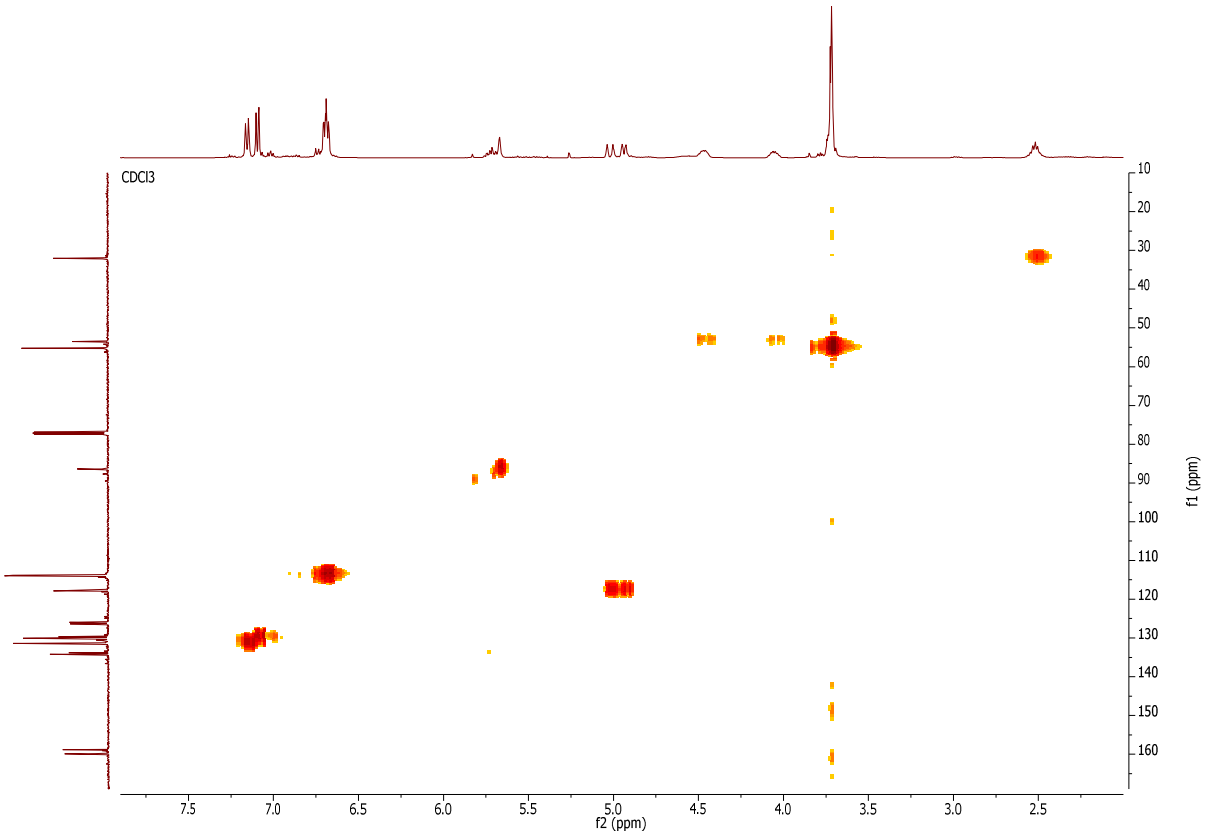

CDCl3
20
40
60
80
100
120
140
160
180
200
f1 (ppm)
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
f2 (ppm)

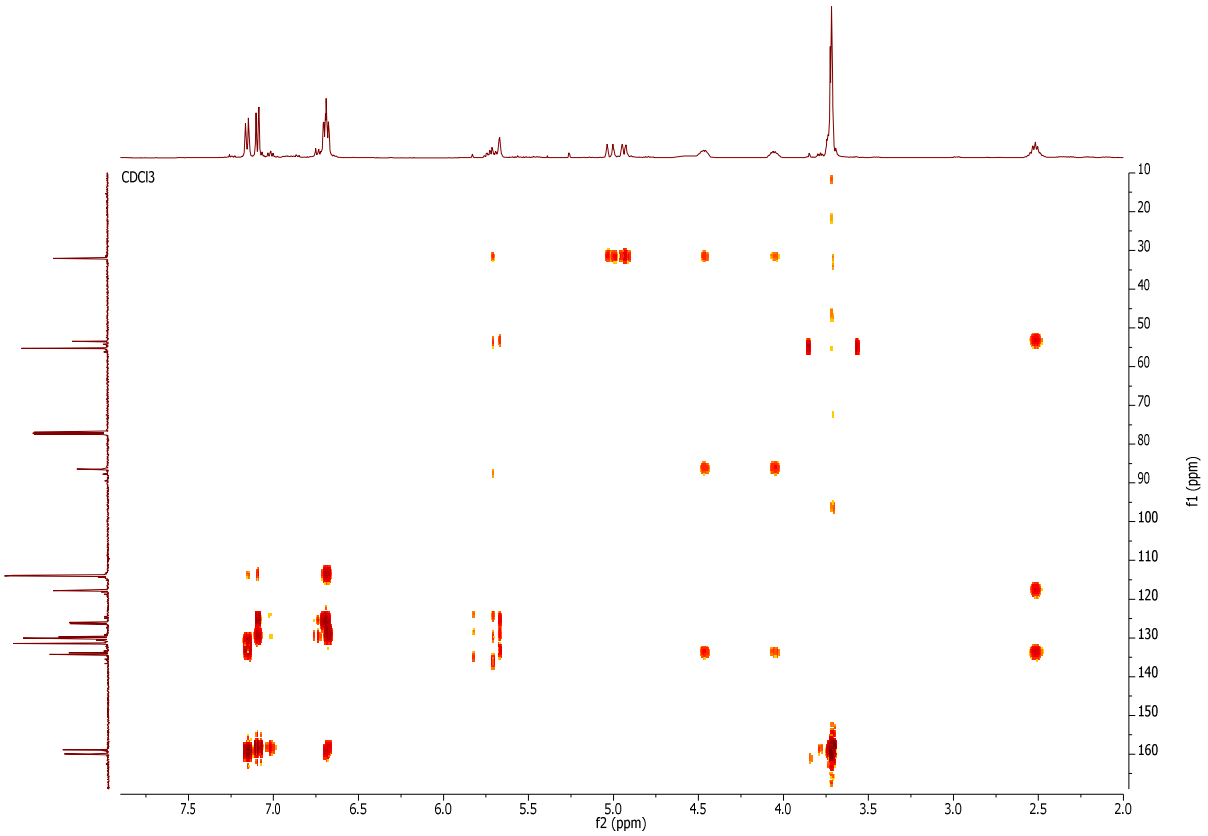

HO
N
S
O
S
O

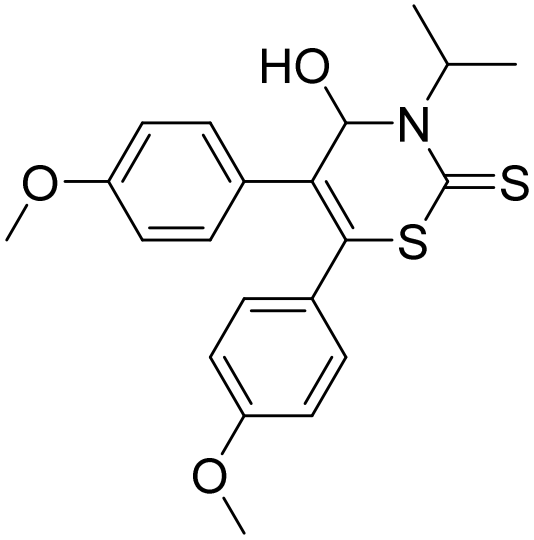
2p


CDCl3
7.17
7.15
7.10
7.09
6.71
6.69
6.68
5.73
5.71
5.69
5.67
5.04
5.00
4.95
4.93
4.58
4.53
4.48
4.46
4.06
4.05
3.73
3.72
2.53
2.52
2.50
1.94
1.94
4.03
1.00
0.92
1.06
1.14
0.67
1.24
0.93
2.98
2.84
2.00
f1 (ppm)

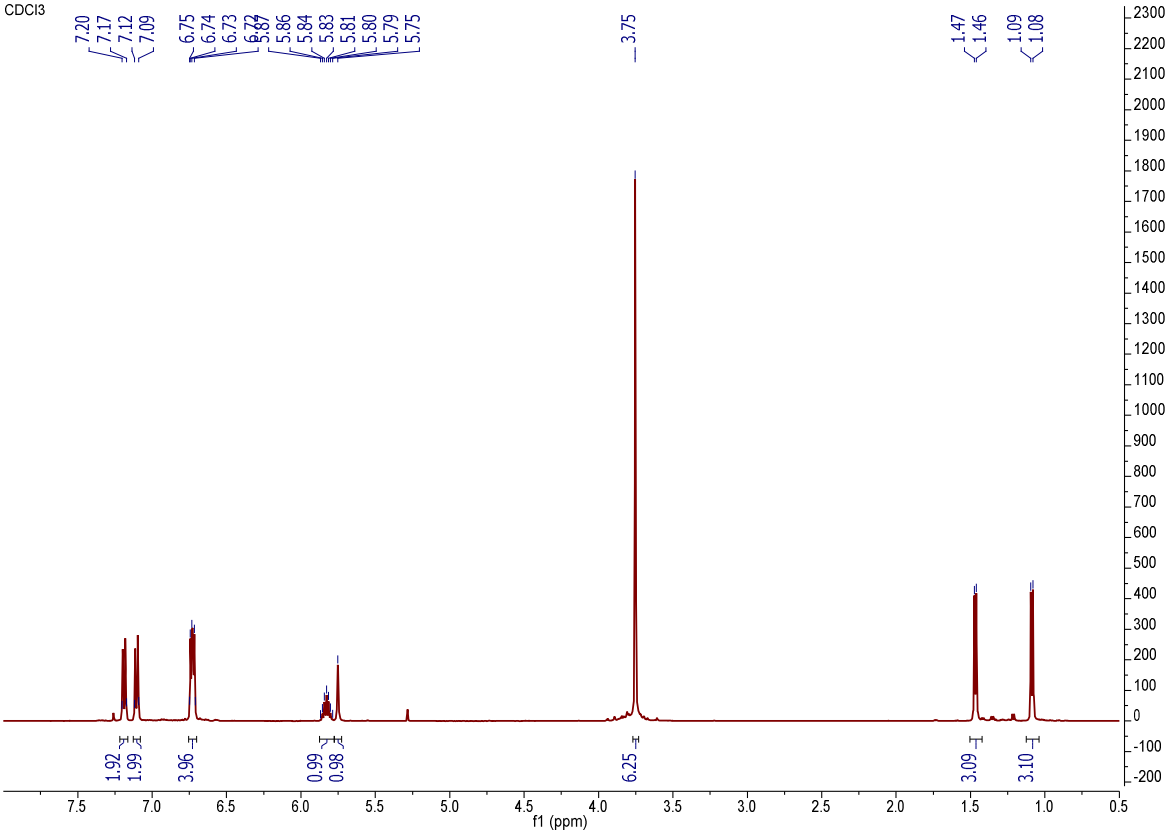

CDCl3
188.70
159.93
158.86
134.24
133.81
131.40
130.05
129.66
126.34
125.98
117.84
113.99
113.83
86.42
55.24
55.20
53.49
32.07
f1 (ppm)

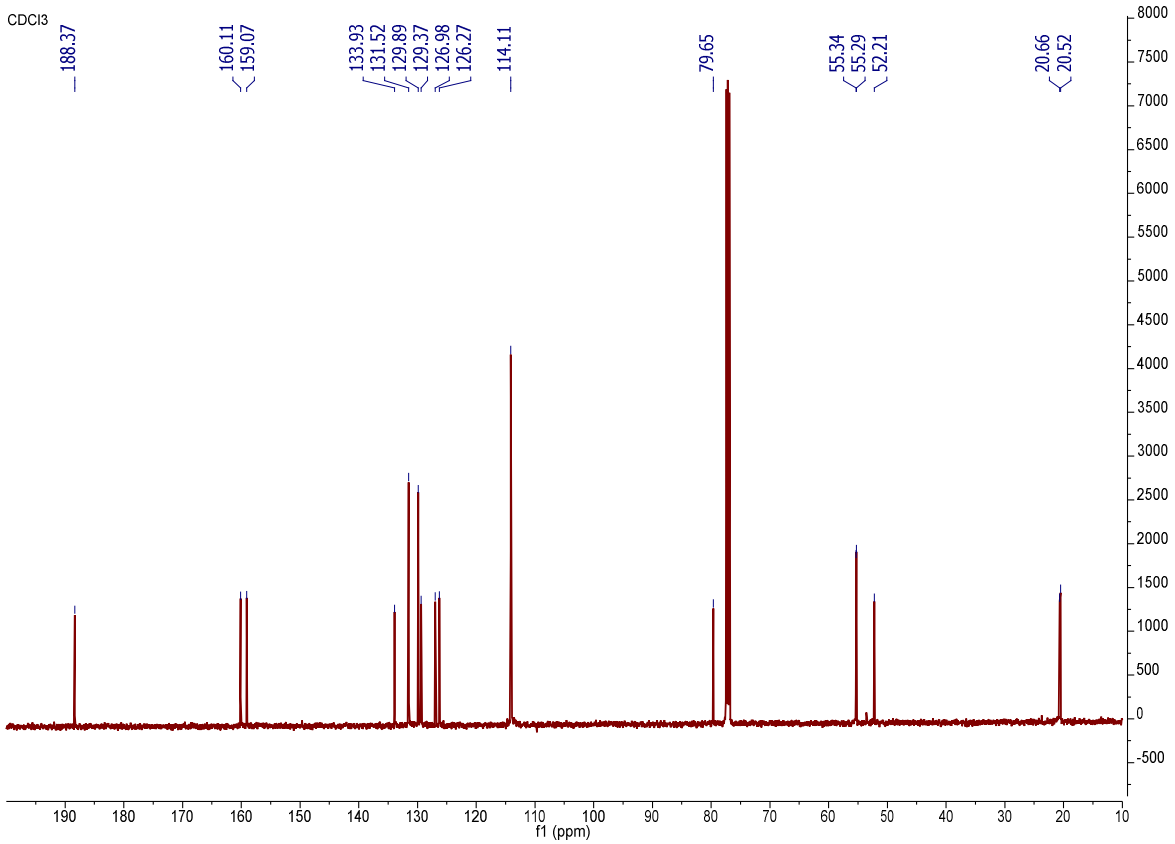

CDCl3
f2 (ppm)
f1 (ppm)

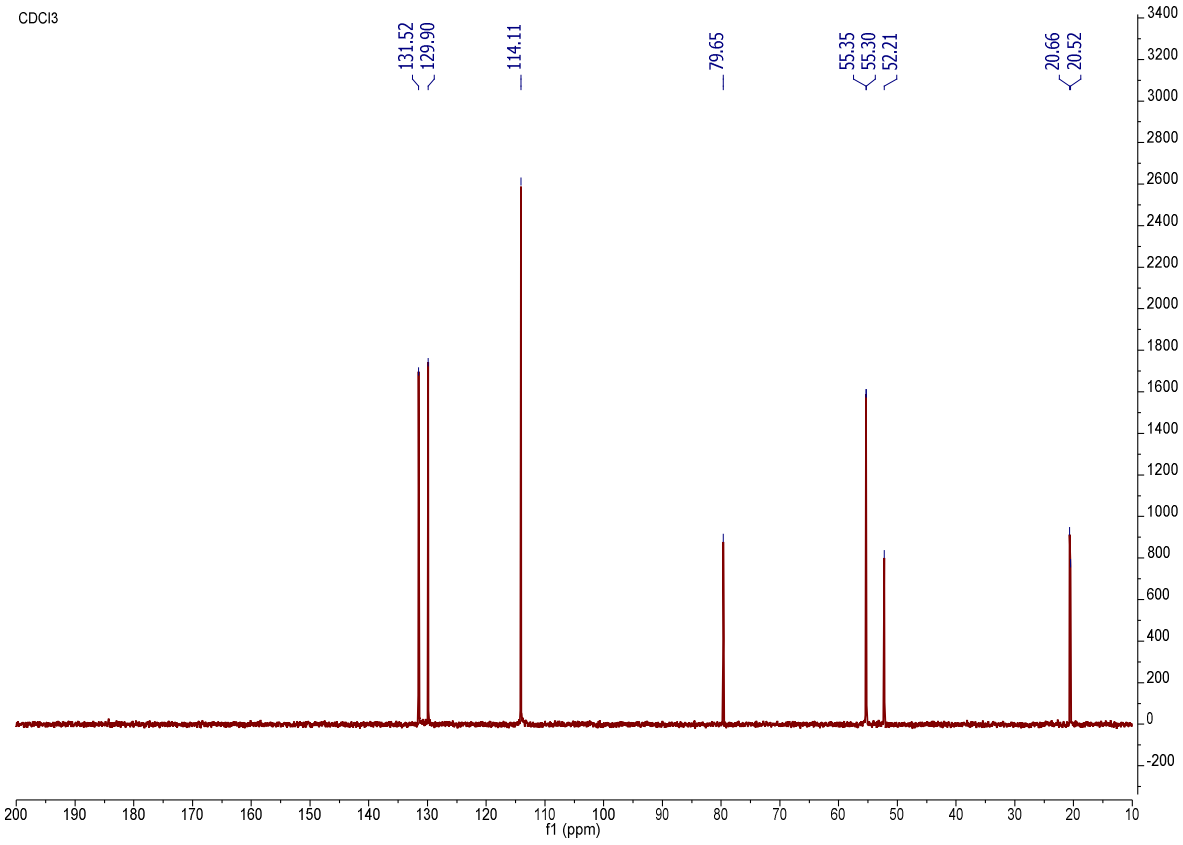

CDCl3
f2 (ppm)
f1 (ppm)

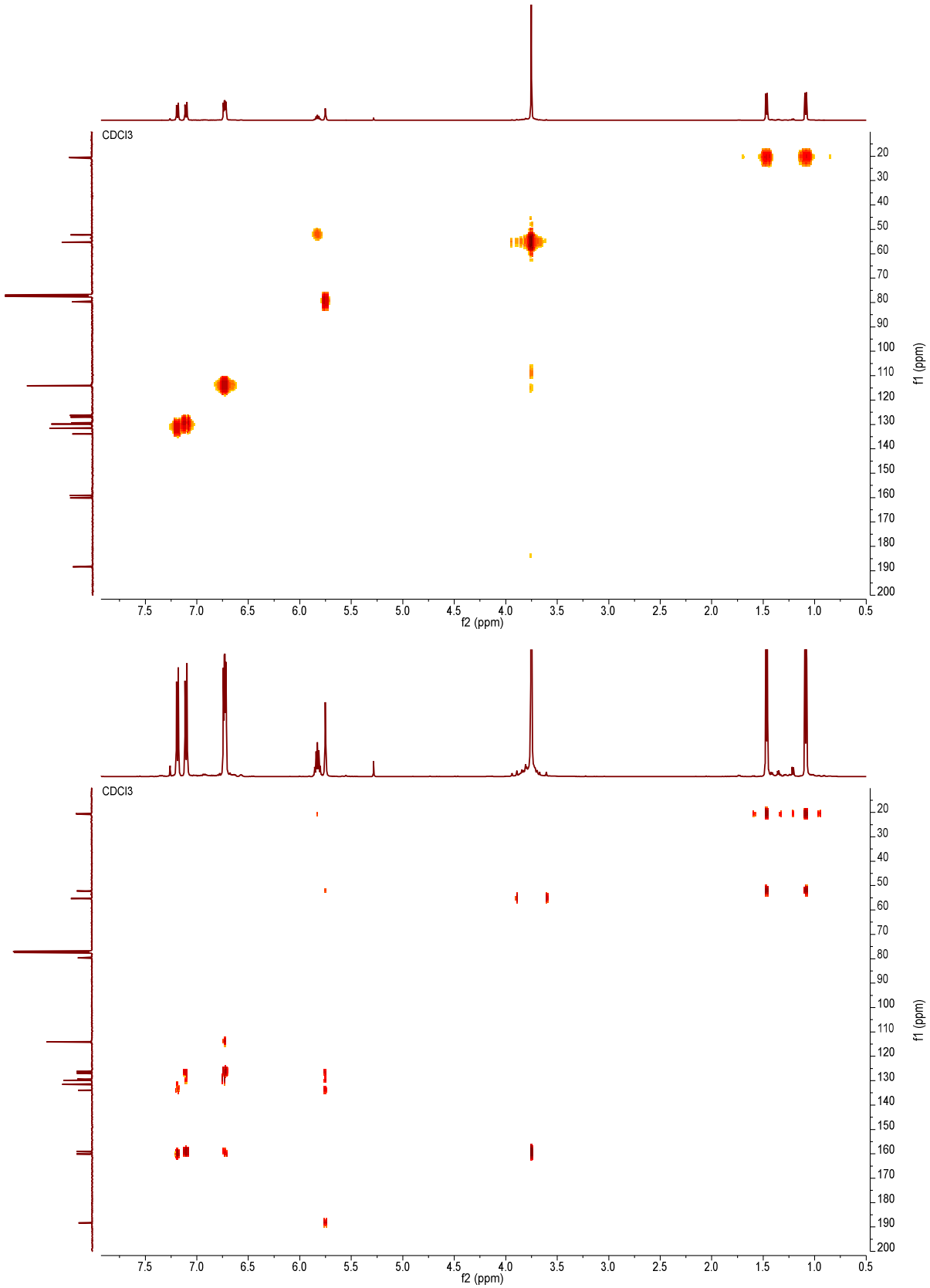

HO
N
S
S
O
O

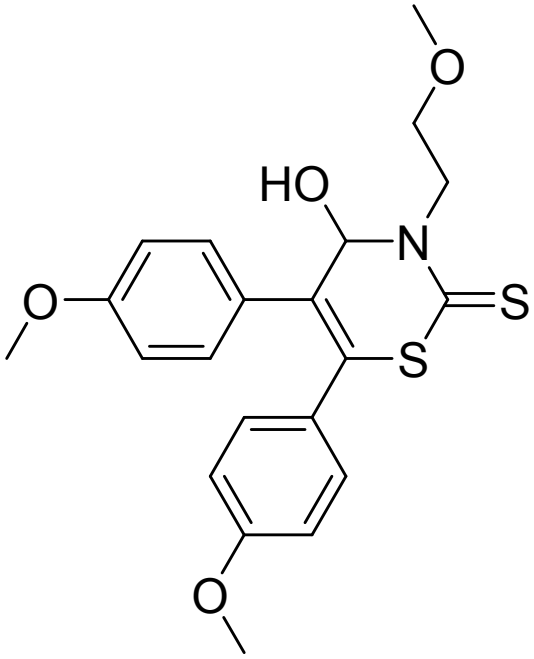
2q


CDCl3
7.20
7.17
7.12
7.09
6.75
6.74
6.73
6.72
5.87
5.86
5.84
5.83
5.81
5.80
5.79
5.75
3.75
1.47
1.46
1.09
1.08
1.92
1.99
3.96
0.99
0.98
6.25
3.09
3.10
f1 (ppm)

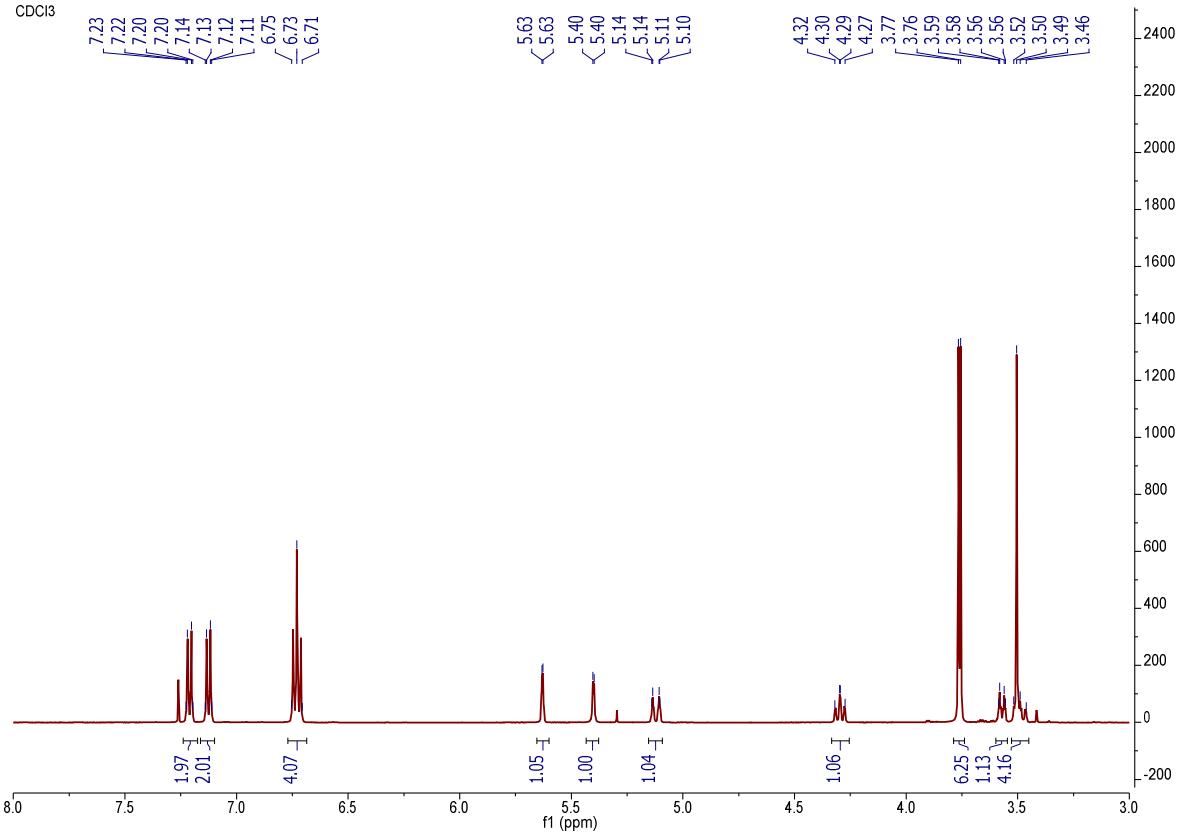

CDCl3
188.37
160.11
159.07
133.93
131.52
129.89
129.37
126.98
126.27
114.11
79.65
55.34
55.29
52.21
20.66
20.52
f1 (ppm)

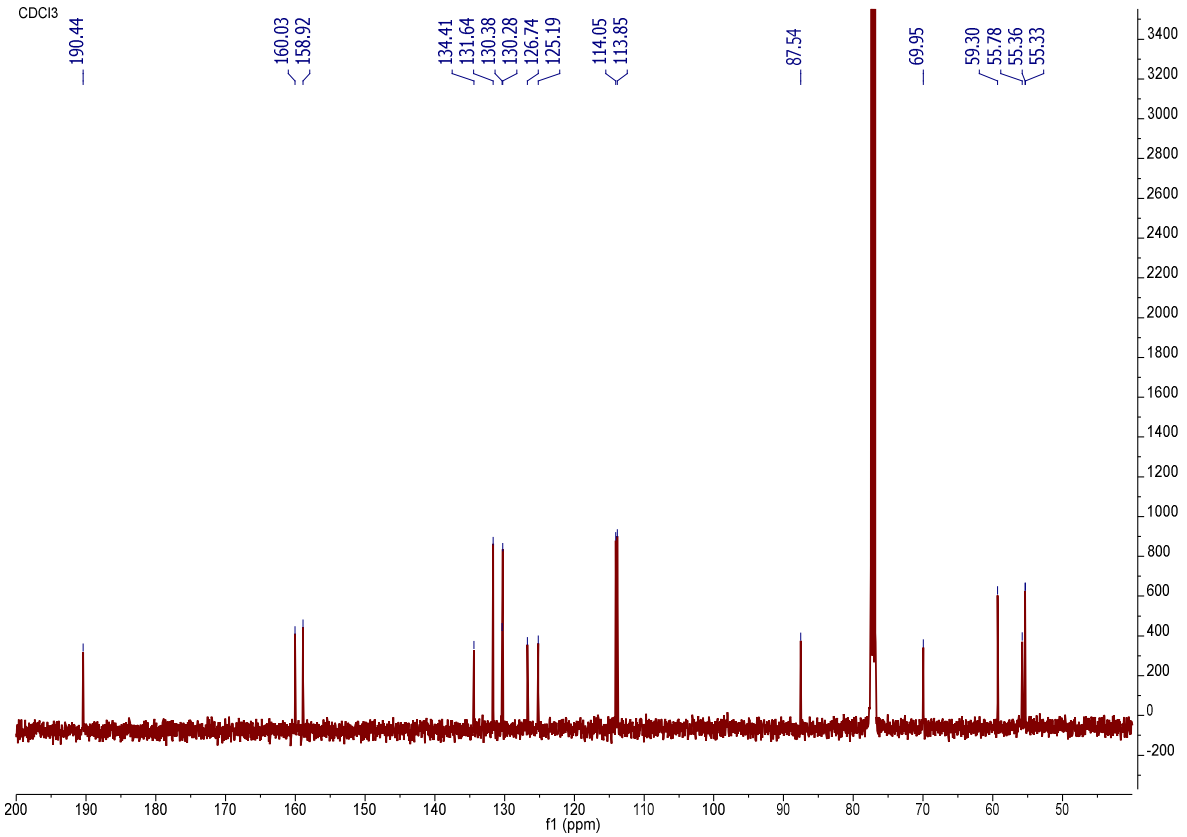

CDCl3
131.52
129.90
114.11
79.65
55.35
55.30
52.21
20.66
20.52
f1 (ppm)

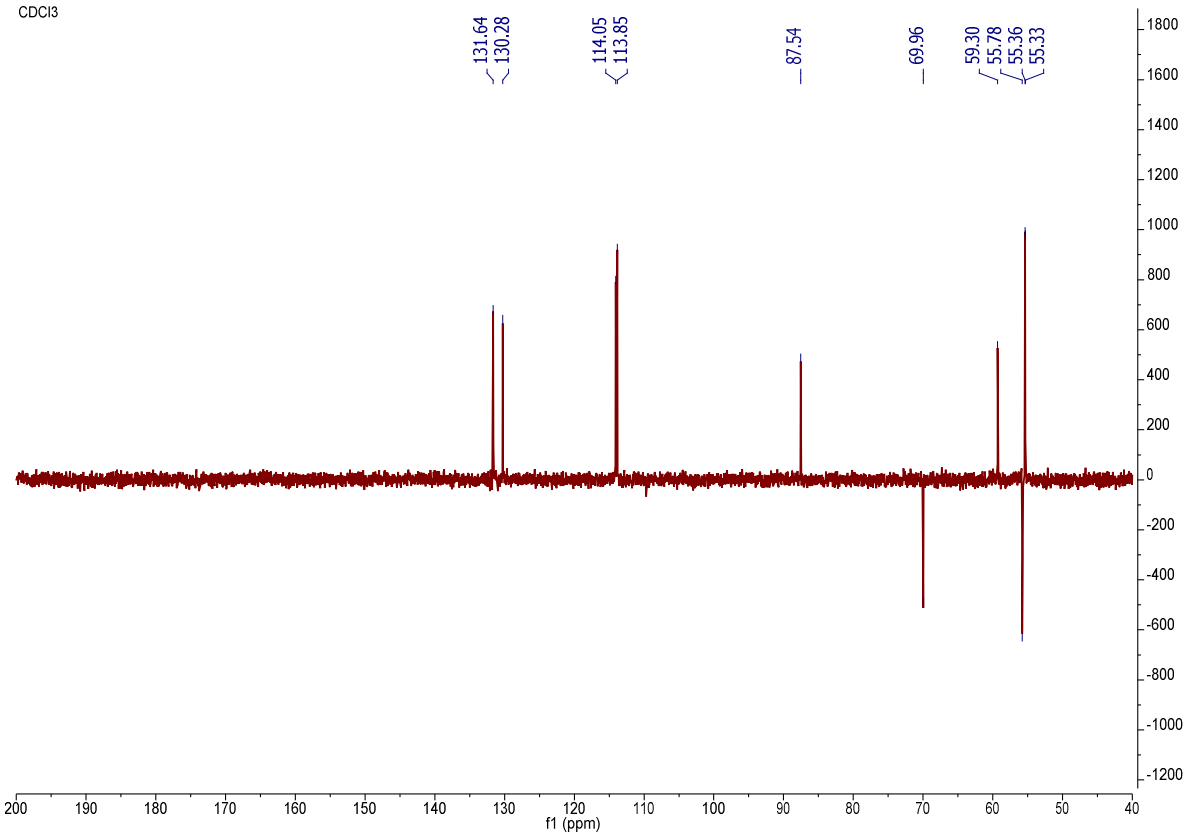

CDCl3
f2 (ppm)
f1 (ppm)
CDCl3
f2 (ppm)
f1 (ppm)

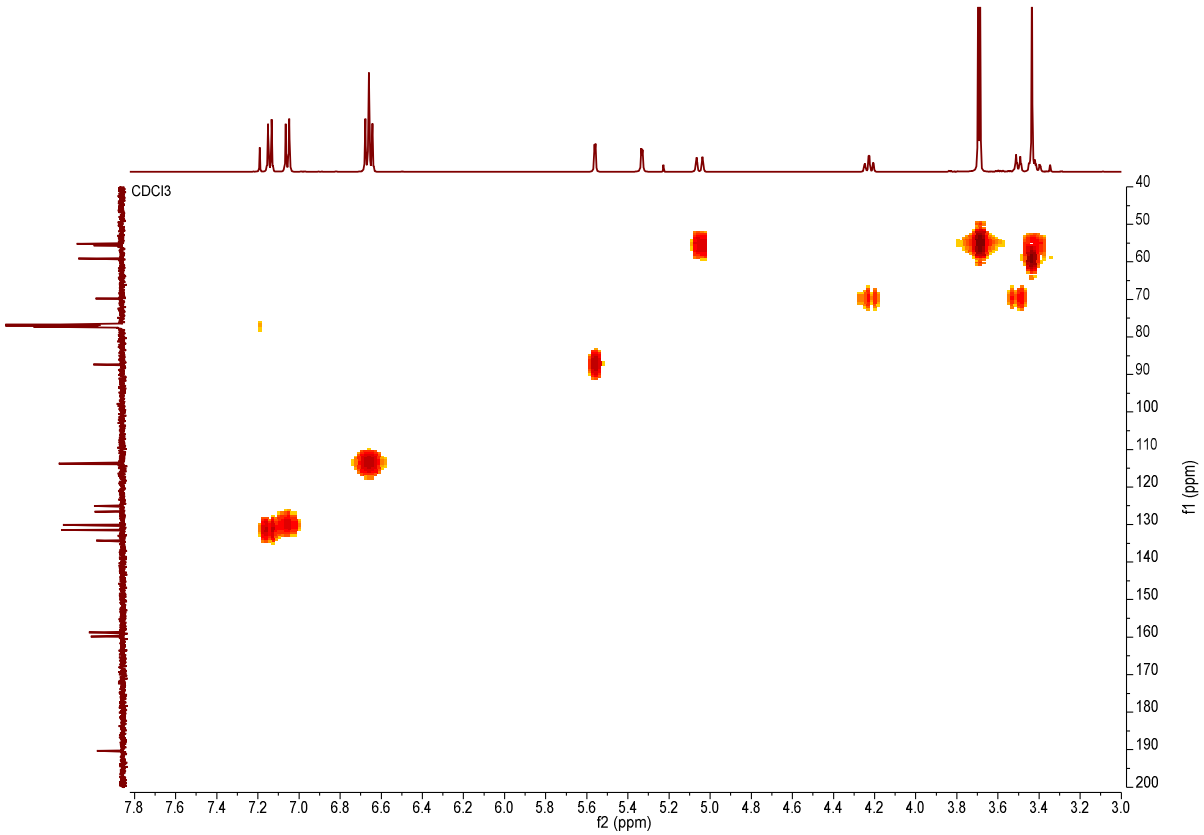

HO
N
O
S
S
O
O

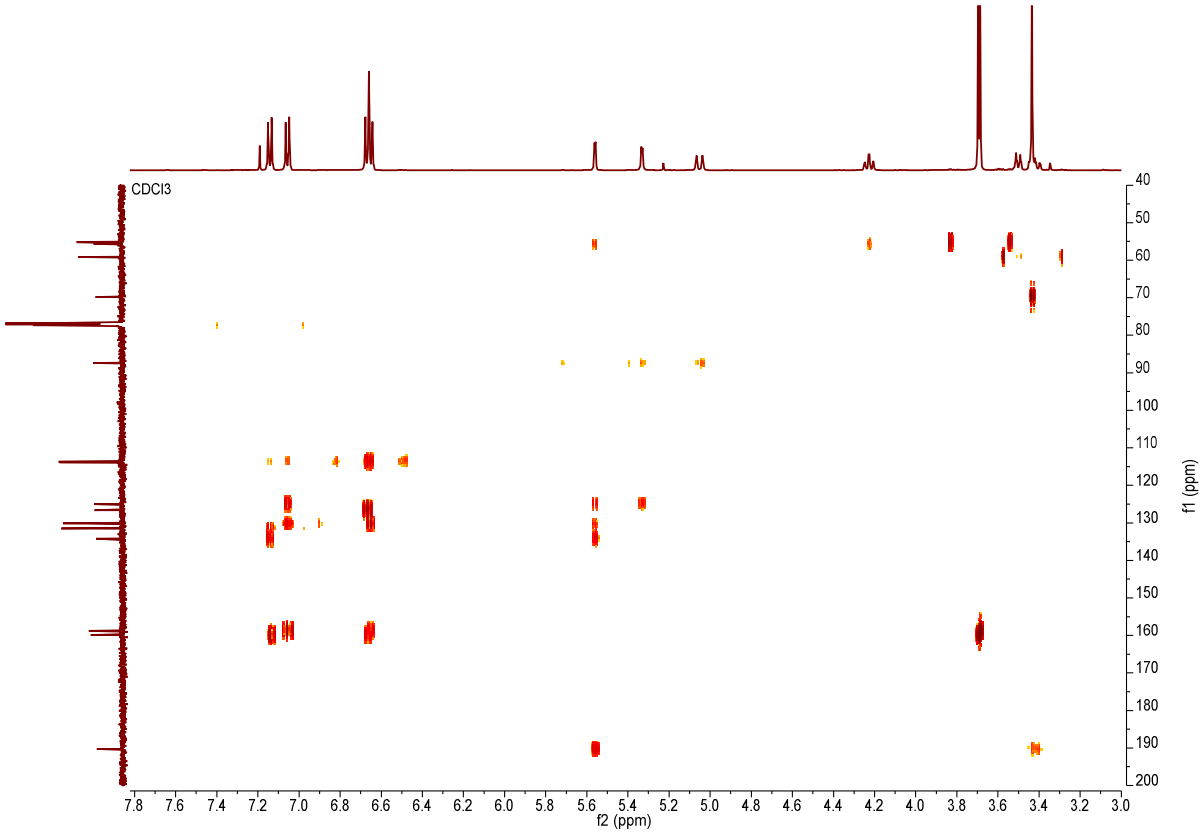
2s

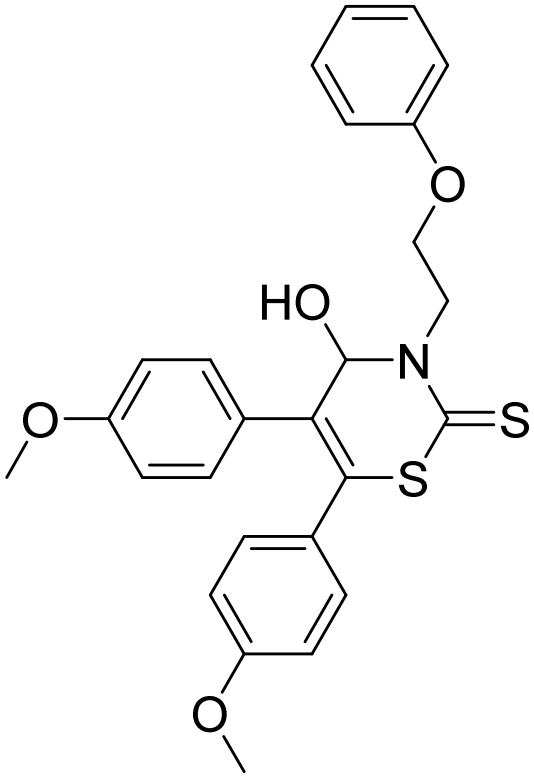

CDCl3
7.23
7.22
7.20
7.20
7.14
7.13
7.12
7.11
6.75
6.73
6.71
5.63
5.63
5.40
5.40
5.14
5.14
5.11
5.10
4.32
4.30
4.29
4.27
3.77
3.76
3.59
3.58
3.56
3.56
3.52
3.50
3.49
3.46
1.97
2.01
4.07
1.05
1.00
1.04
1.06
6.25
1.13
4.16
f1 (ppm)


CDCl3
190.44
160.03
158.92
134.41
131.64
130.38
130.28
126.74
125.19
114.05
113.85
87.54
69.95
59.30
55.78
55.36
55.33
f1 (ppm)

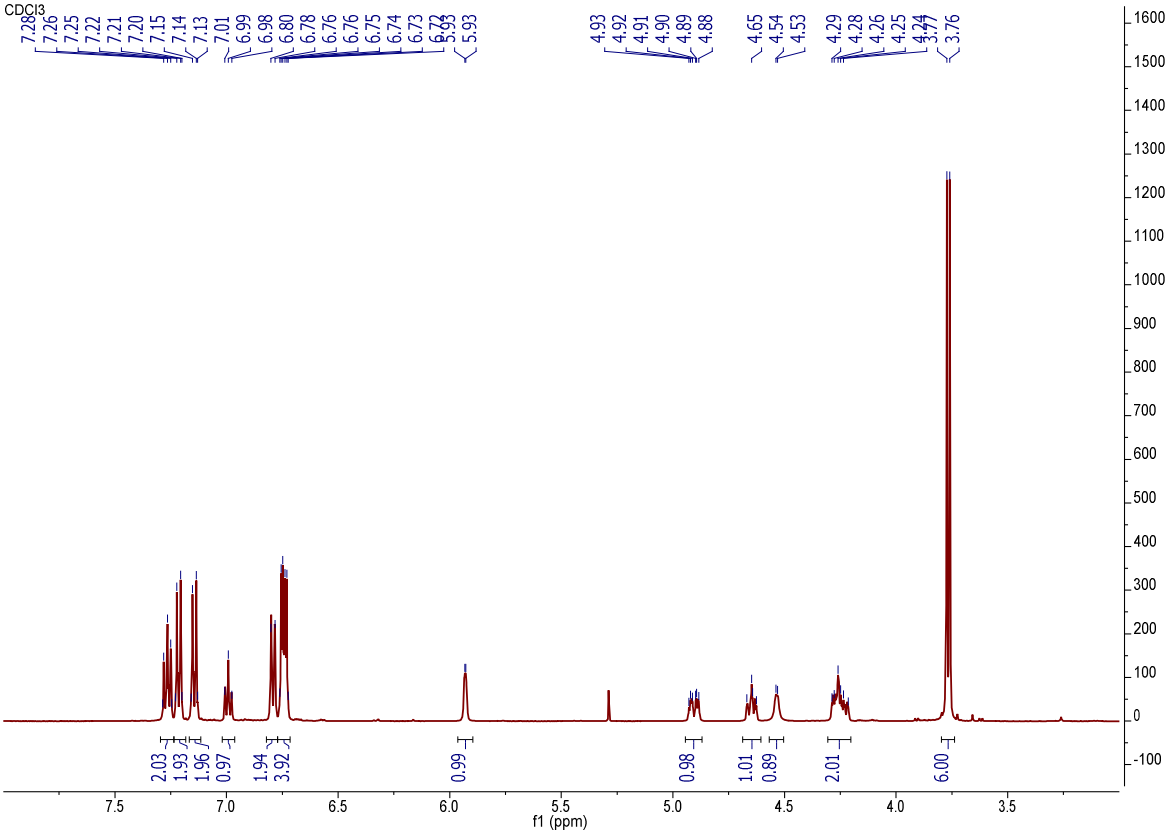

CDCl3
131.64
130.28
114.05
113.85
87.54
69.96
59.30
55.78
55.36
55.33
f1 (ppm)

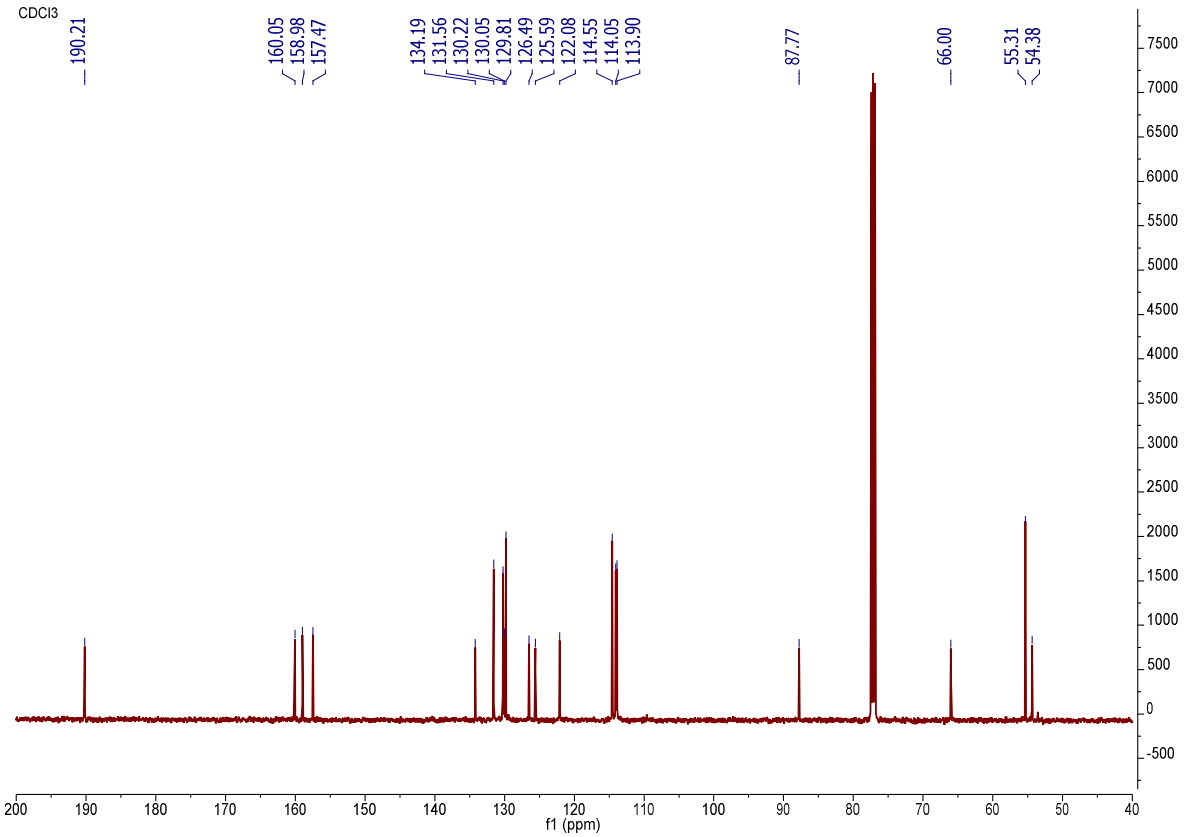

CDCl3
f1 (ppm)
f2 (ppm)

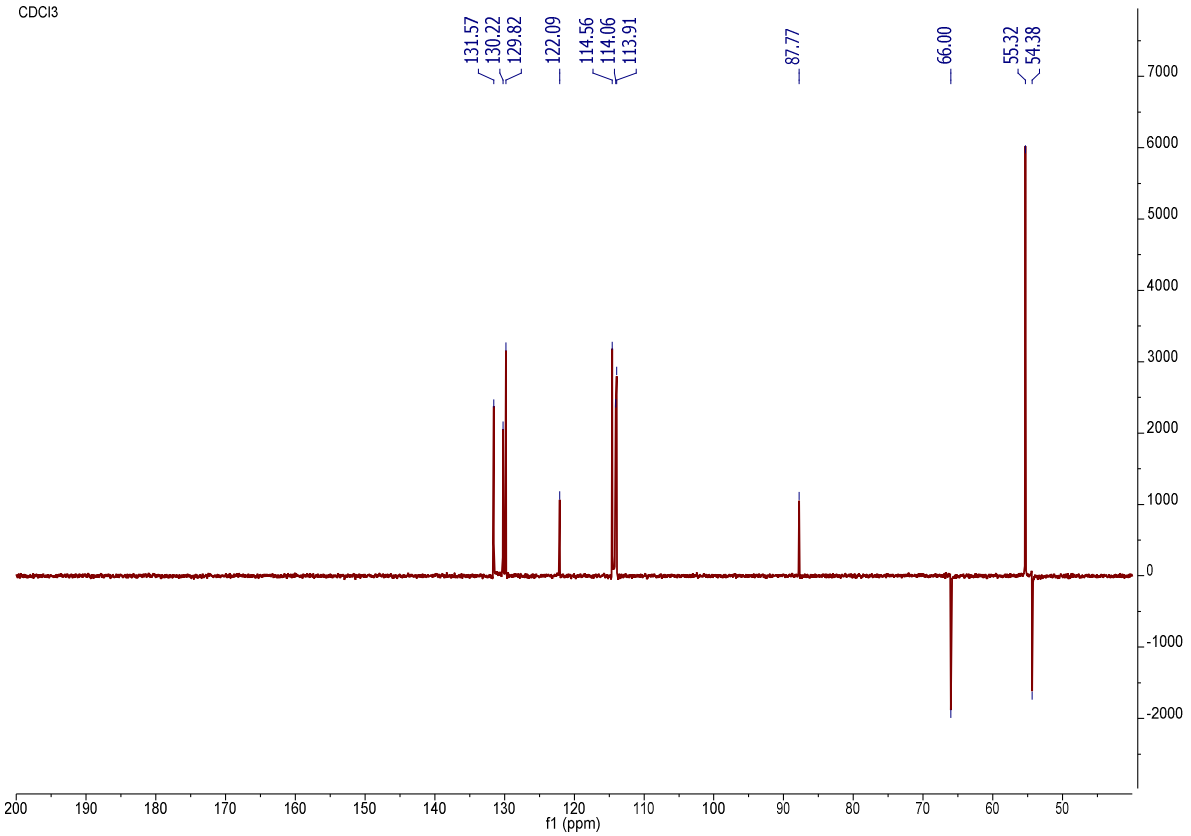

CDCl3
f1 (ppm)
f2 (ppm)

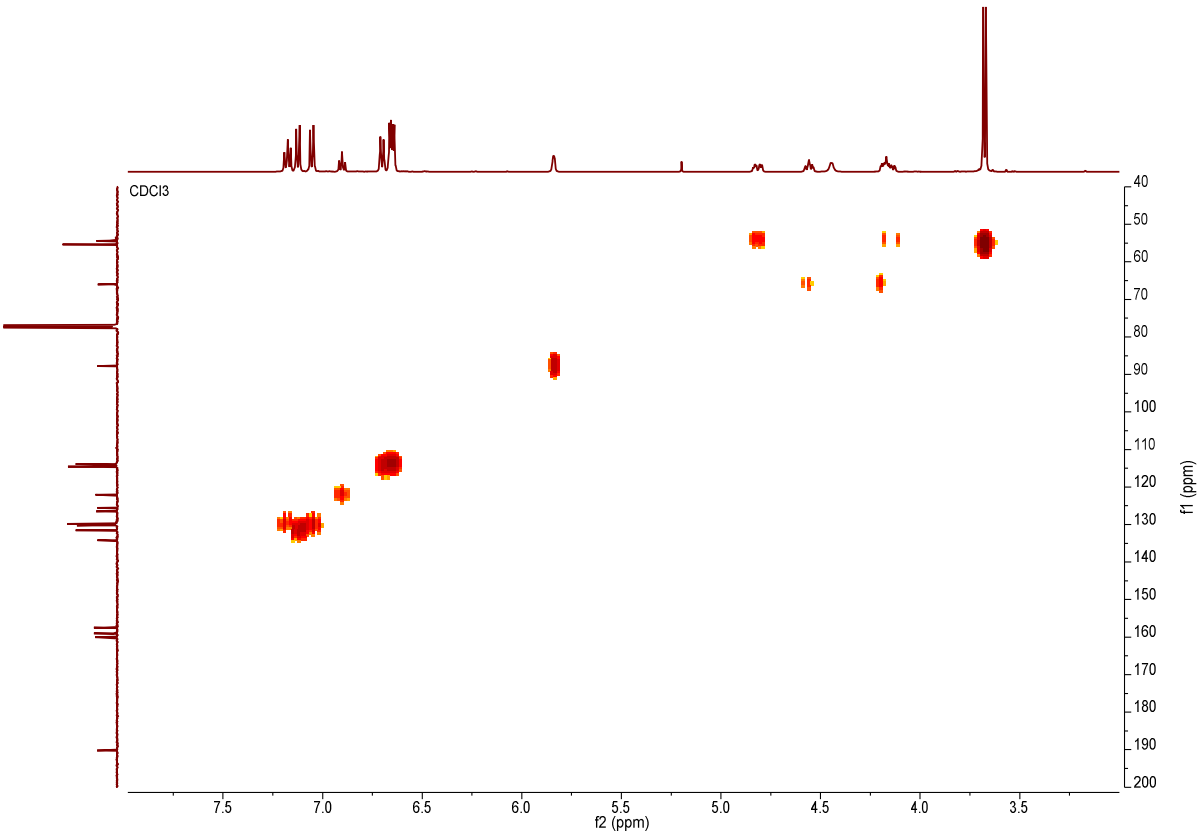

HO
N
O
S
S
O
O

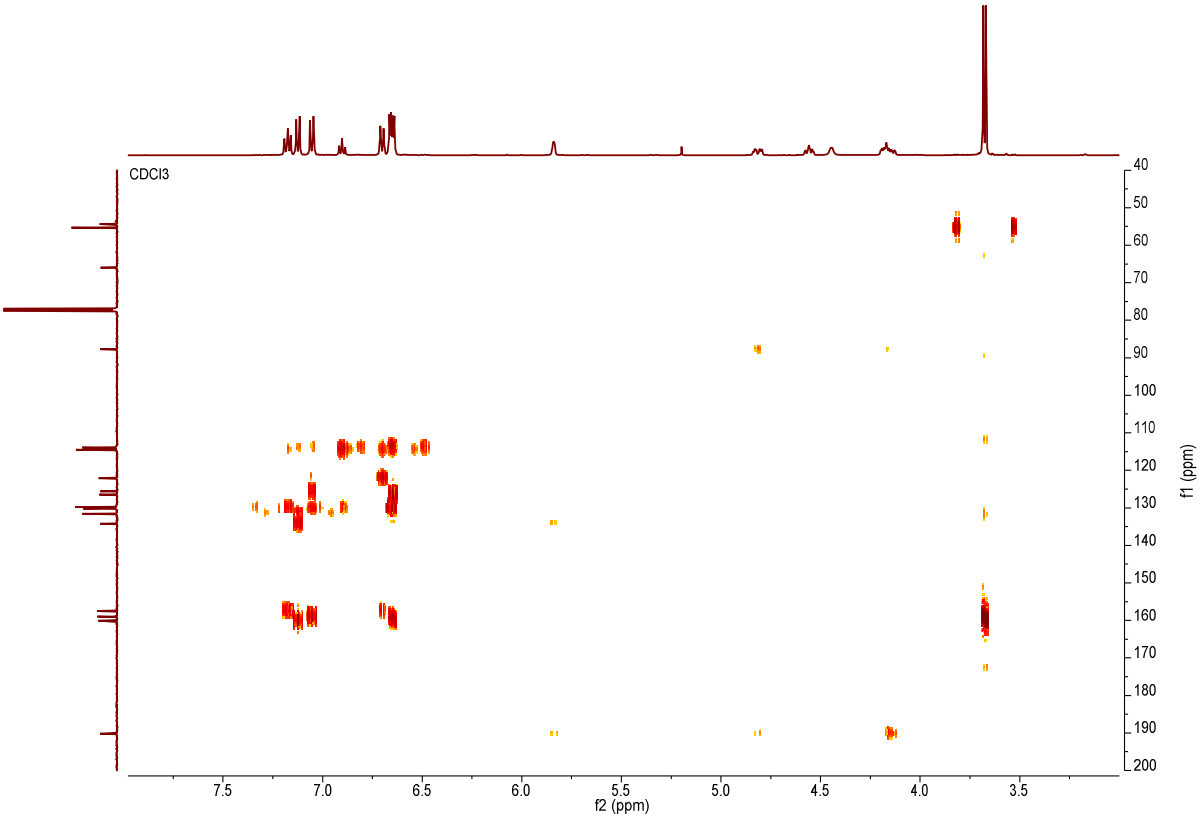
2t

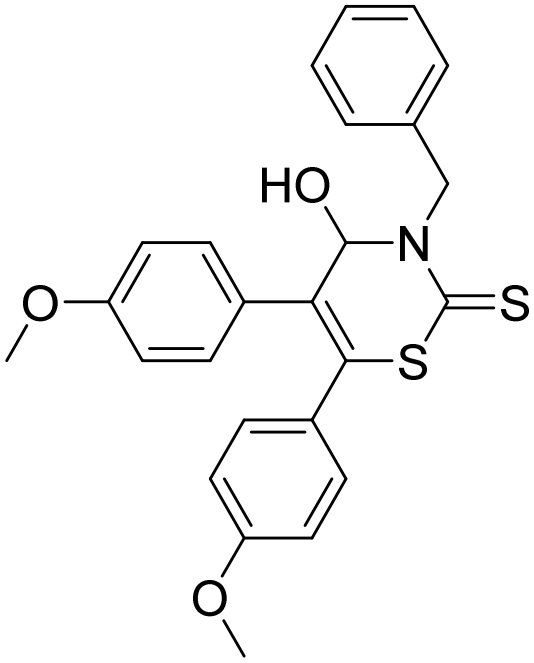

CDCl3
7.28
7.26
7.25
7.22
7.21
7.20
7.15
7.14
7.13
7.01
6.99
6.98
6.80
6.78
6.76
6.76
6.75
6.74
6.73
5.93
5.93
4.93
4.92
4.91
4.90
4.89
4.88
4.65
4.54
4.53
4.29
4.28
4.26
4.25
3.76
2.03
1.93
1.96
0.97
1.94
3.92
0.99
0.98
1.01
0.89
2.01
6.00
f1 (ppm)


CDCl3
190.21
160.05
158.98
157.47
134.19
131.56
130.22
130.05
129.81
126.49
125.59
122.08
114.55
114.05
113.90
87.77
66.00
55.31
54.38
f1 (ppm)

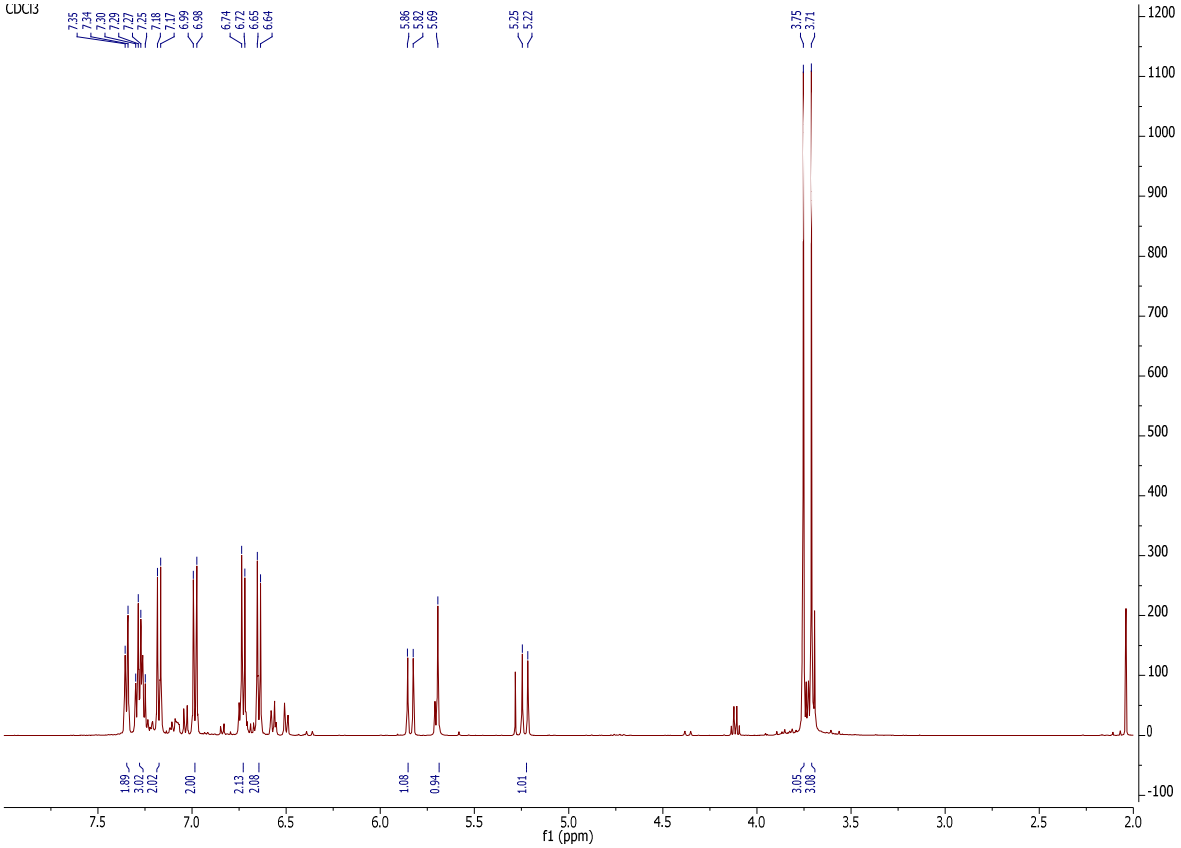

CDCl3
131.57
130.22
129.82
122.09
114.56
114.06
113.91
87.77
66.00
55.32
54.38
f1 (ppm)

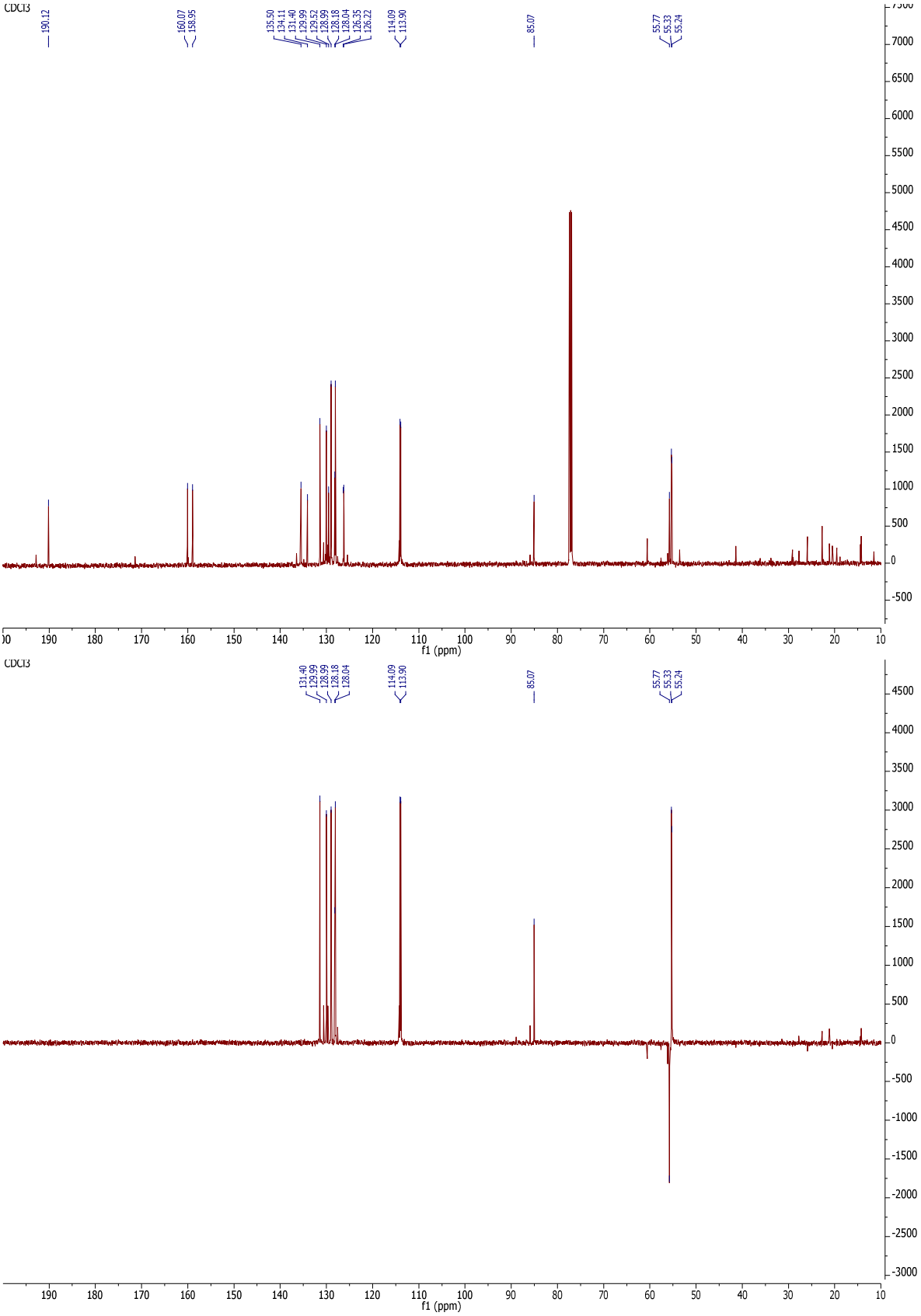

CDCl3
f2 (ppm)
f1 (ppm)

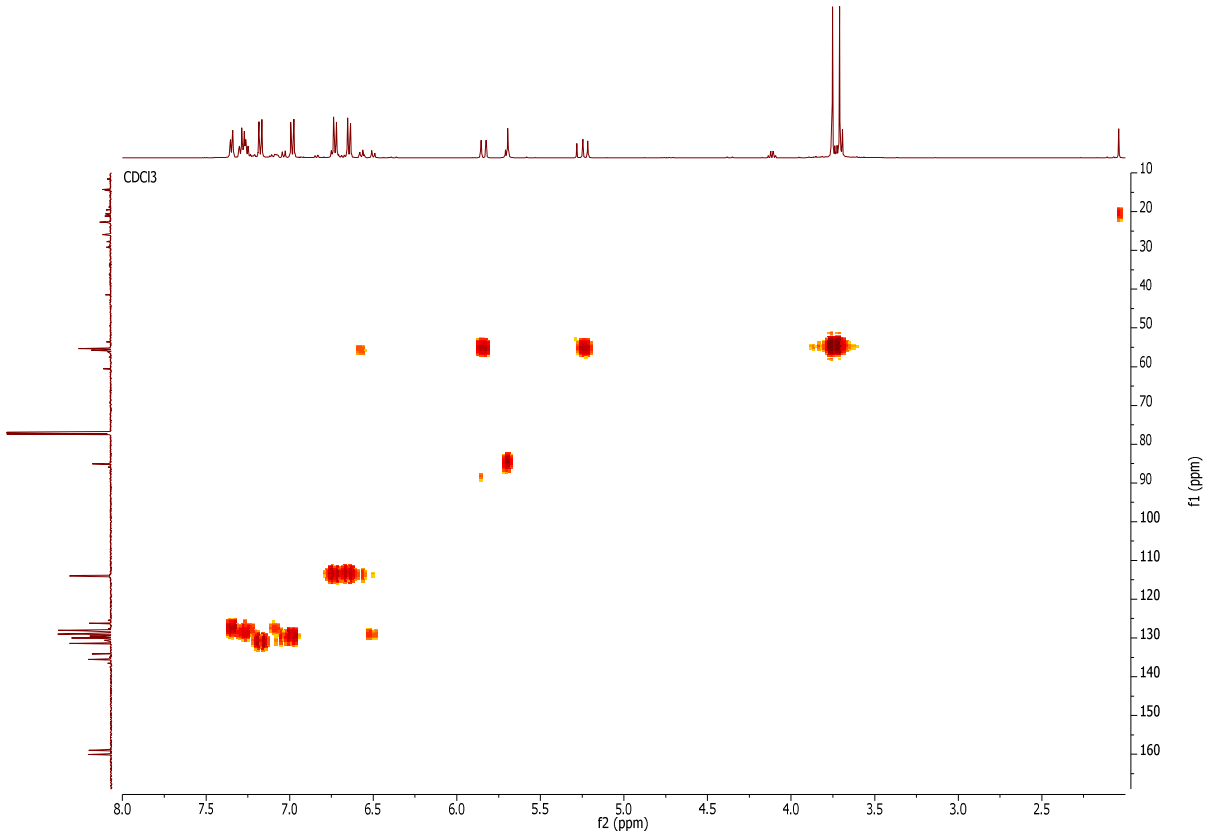

CDCl3
f2 (ppm)
f1 (ppm)

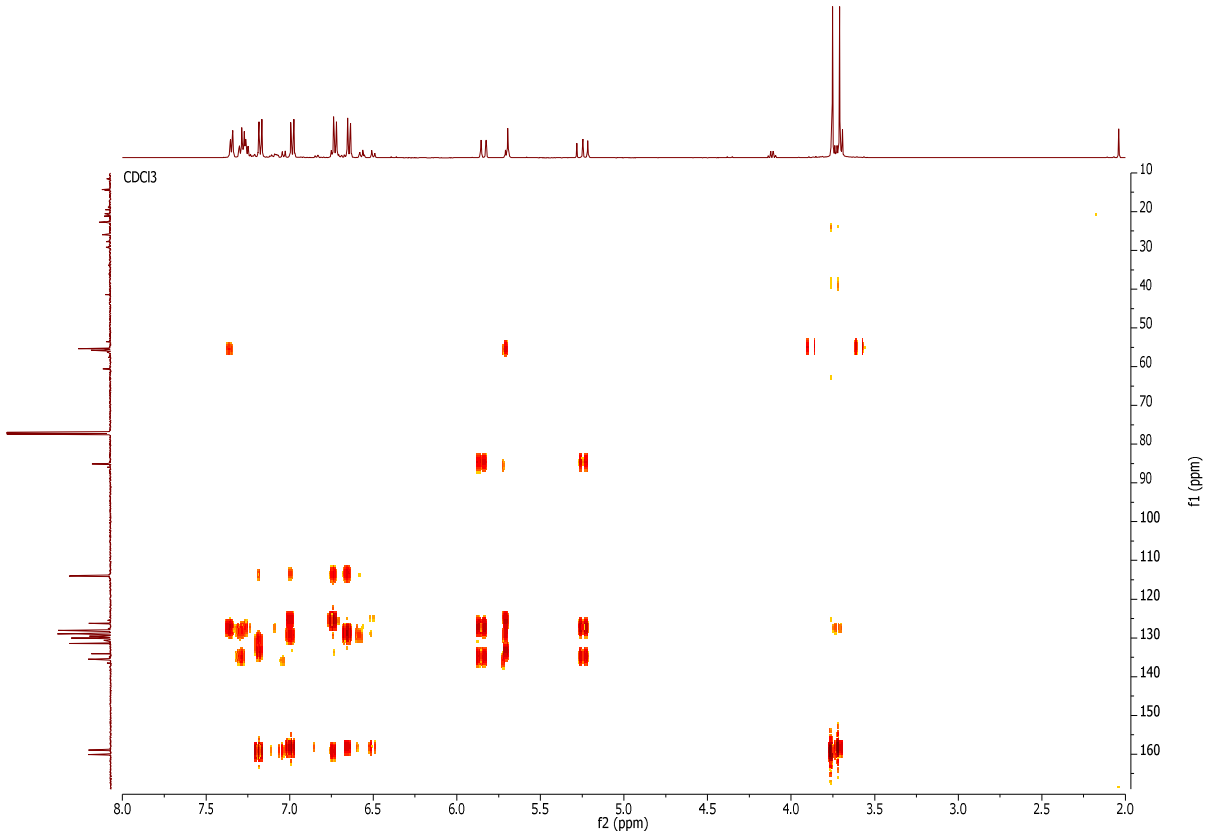

HO
N
O
S
S
O

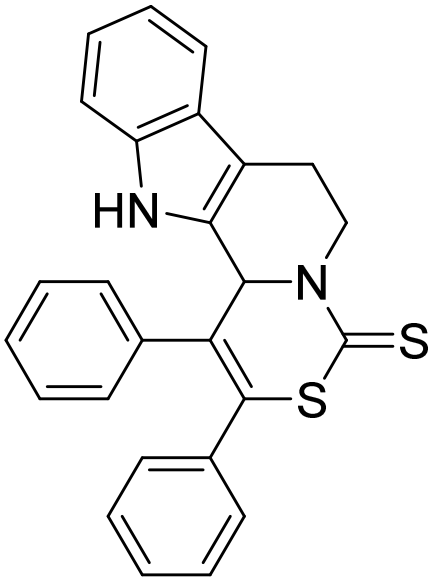
2u


CDCl3
7.35
7.34
7.30
7.29
7.27
7.25
7.18
7.17
6.99
6.98
6.74
6.72
6.65
6.64
5.86
5.82
5.69
5.25
5.22
3.75
3.71
1.89
3.02
2.02
2.00
2.13
2.08
1.08
0.94
1.01
3.05
3.08
f1 (ppm)

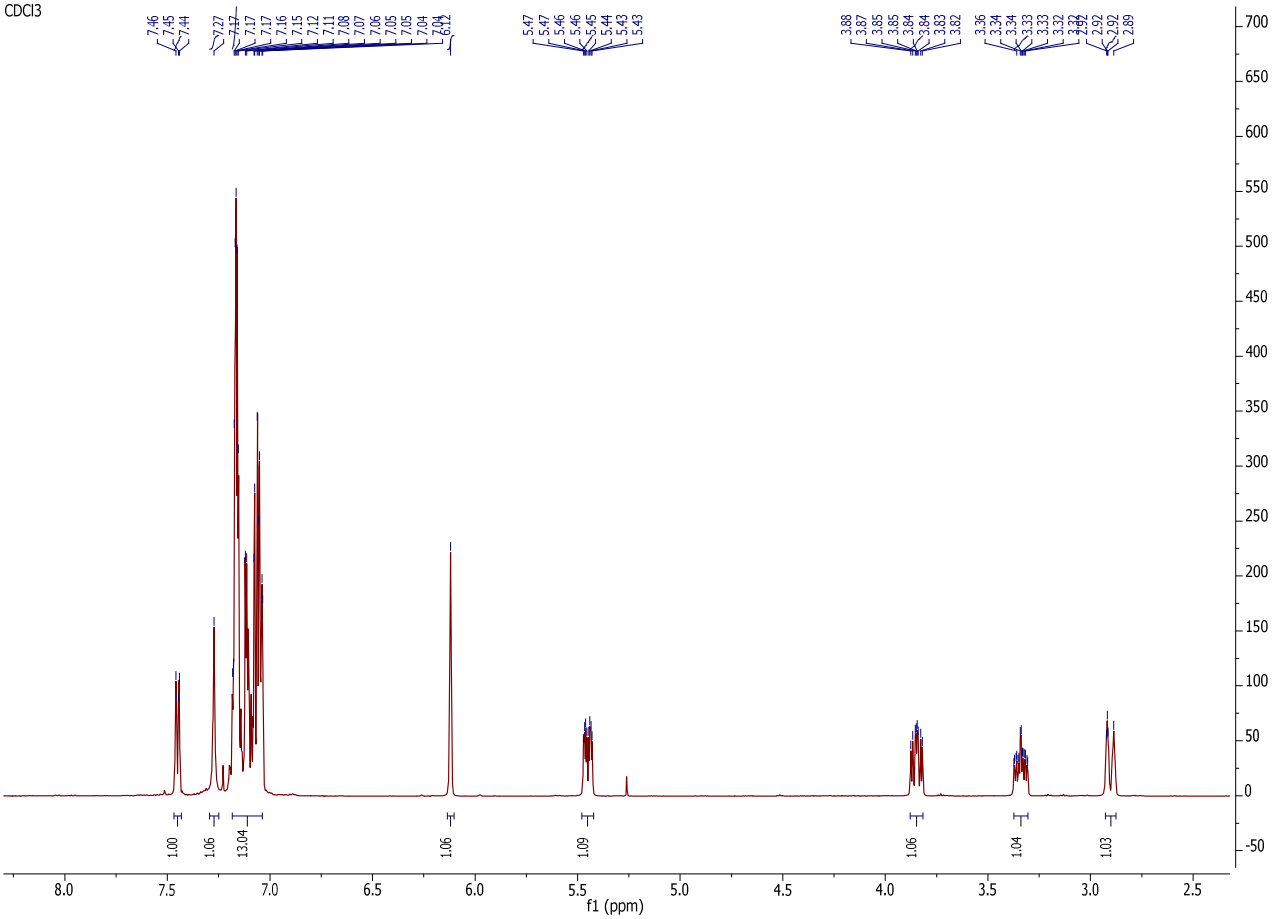

CDCl3
190.12
160.07
158.95
135.50
134.11
131.40
129.99
129.52
128.99
128.18
128.04
126.35
126.22
114.09
113.90
85.07
55.77
55.33
55.24
f1 (ppm)
CDCl3
131.40
129.99
128.99
128.18
128.04
114.09
113.90
85.07
55.77
55.33
55.24
f1 (ppm)

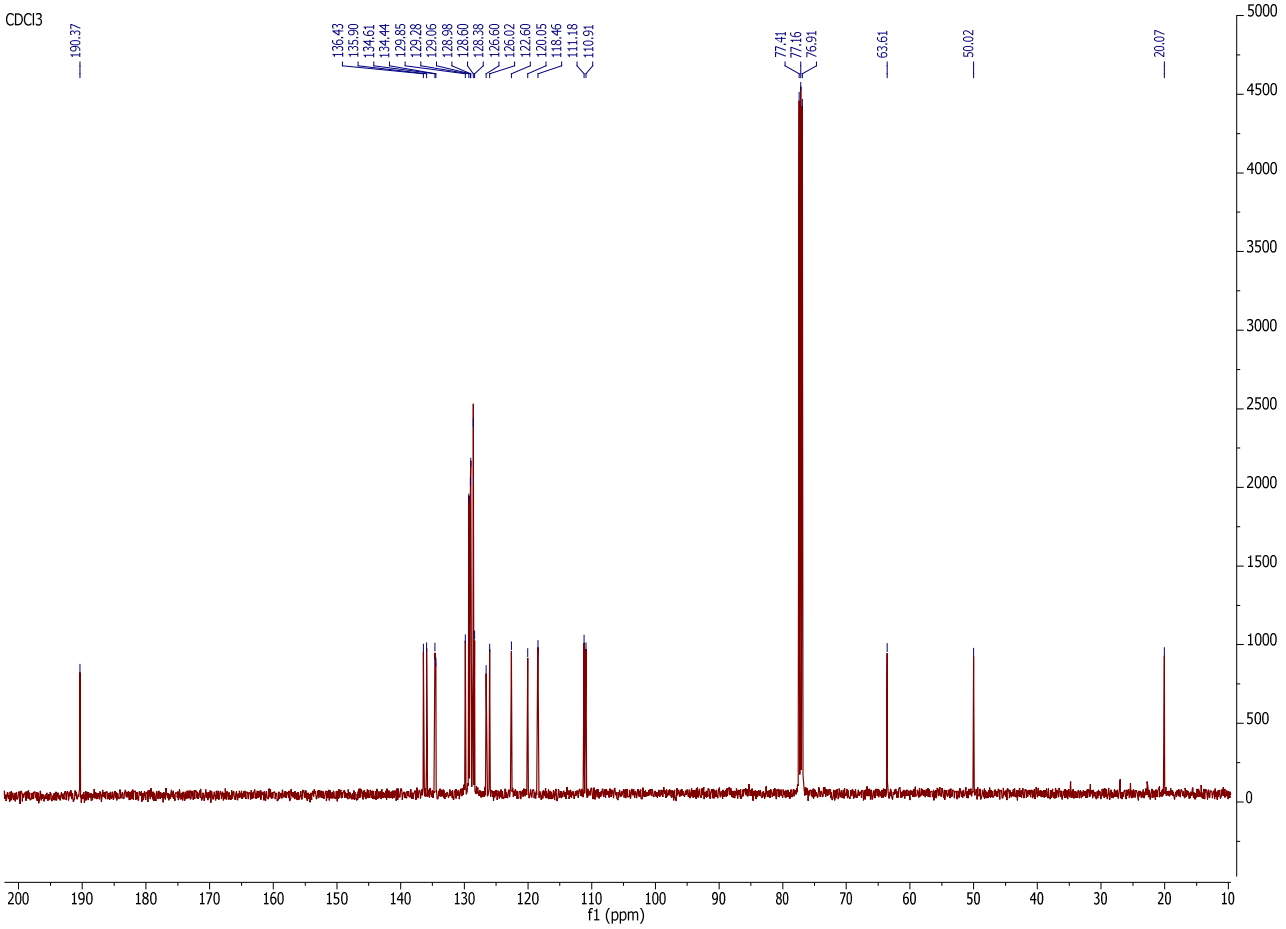

CDCl3
f2 (ppm)
f1 (ppm)

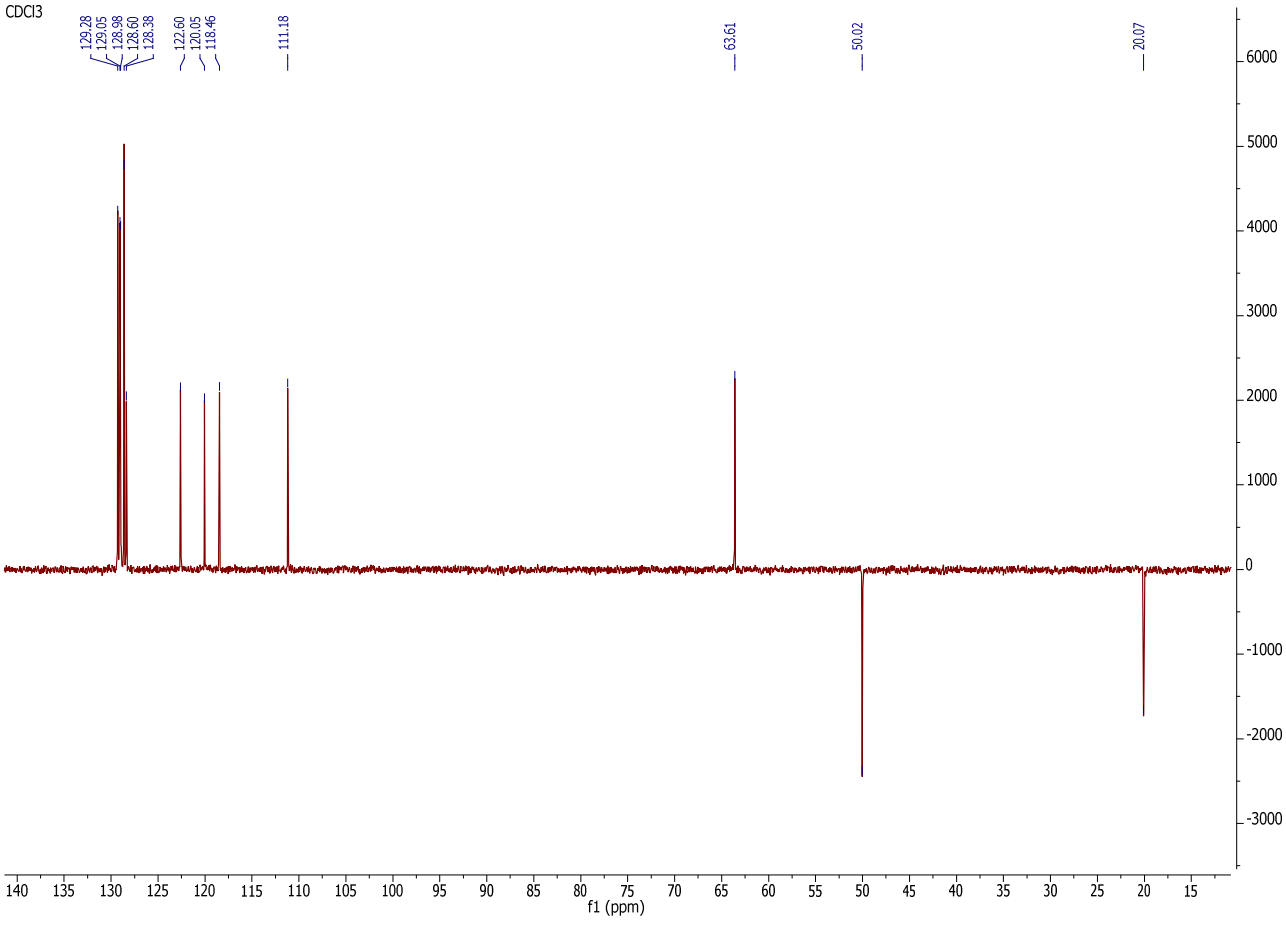

CDCl3
f2 (ppm)
f1 (ppm)

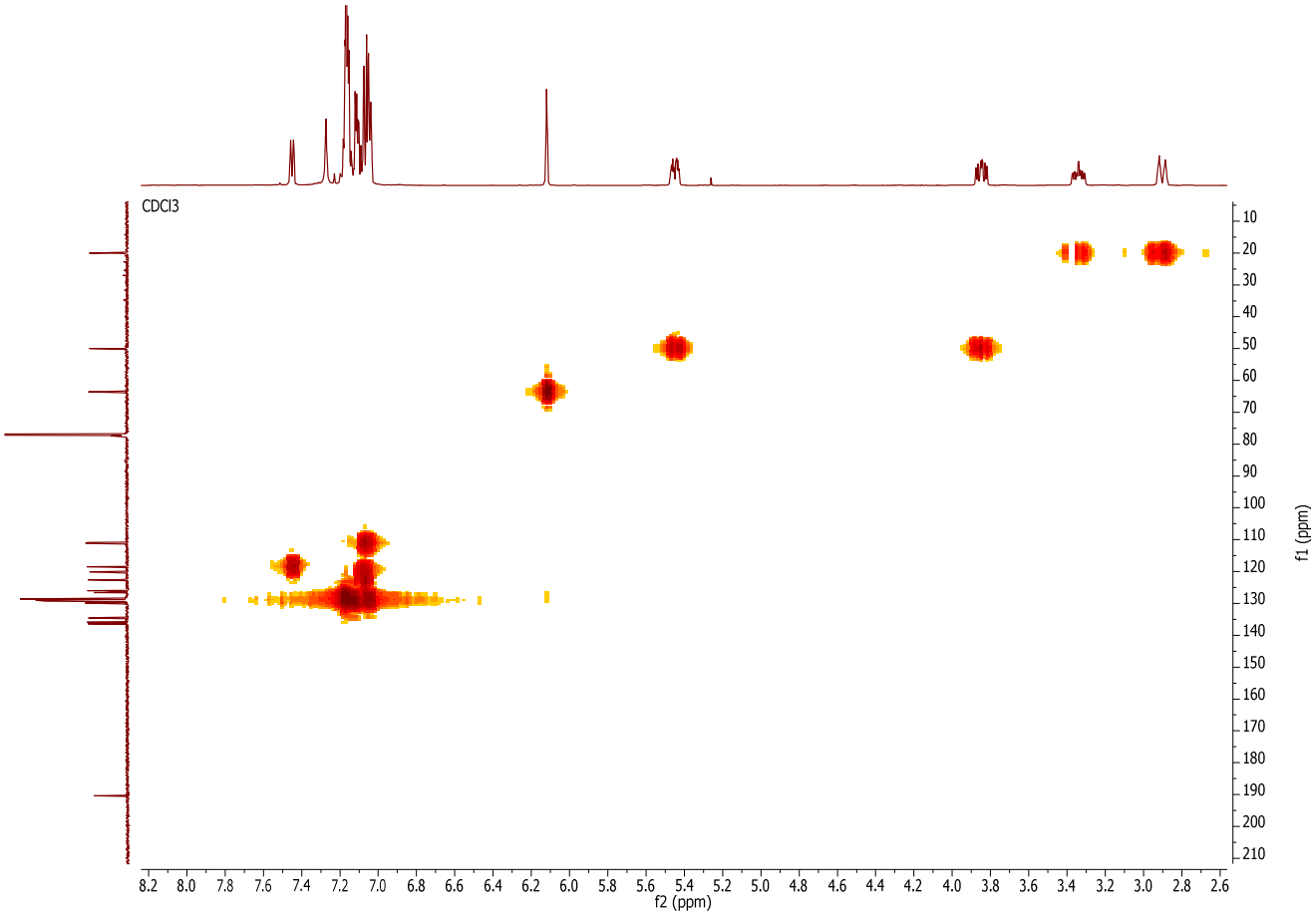


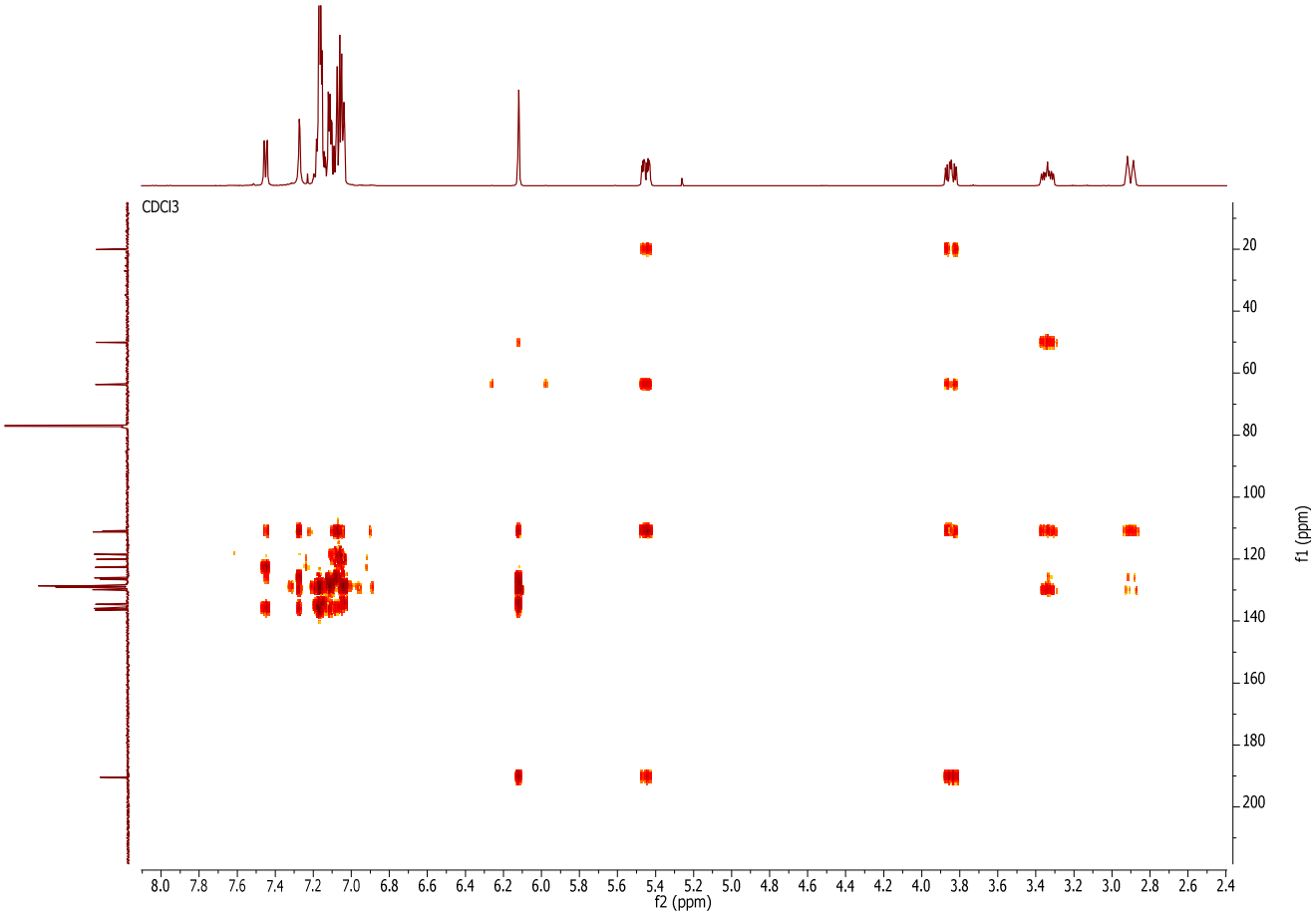
3a

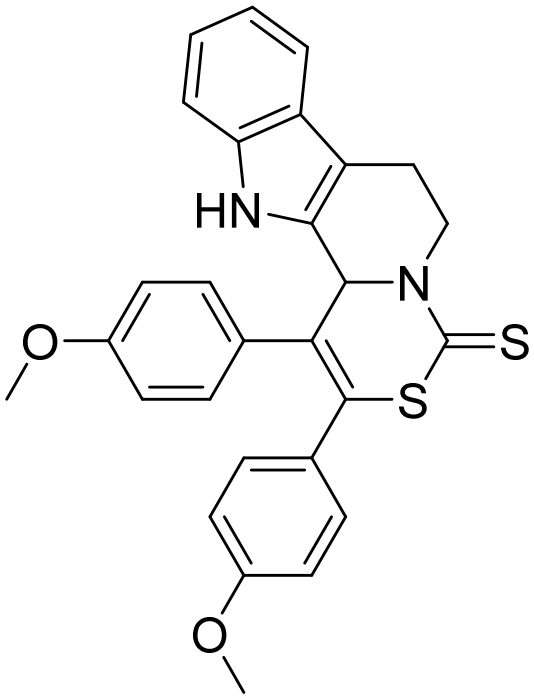



CDCl3
190.37
136.43
135.90
134.61
134.44
129.85
129.28
129.06
128.98
128.60
128.38
126.60
126.02
122.60
120.05
118.46
111.18
110.91
77.41
77.16
76.91
63.61
50.02
20.07
f1 (ppm)

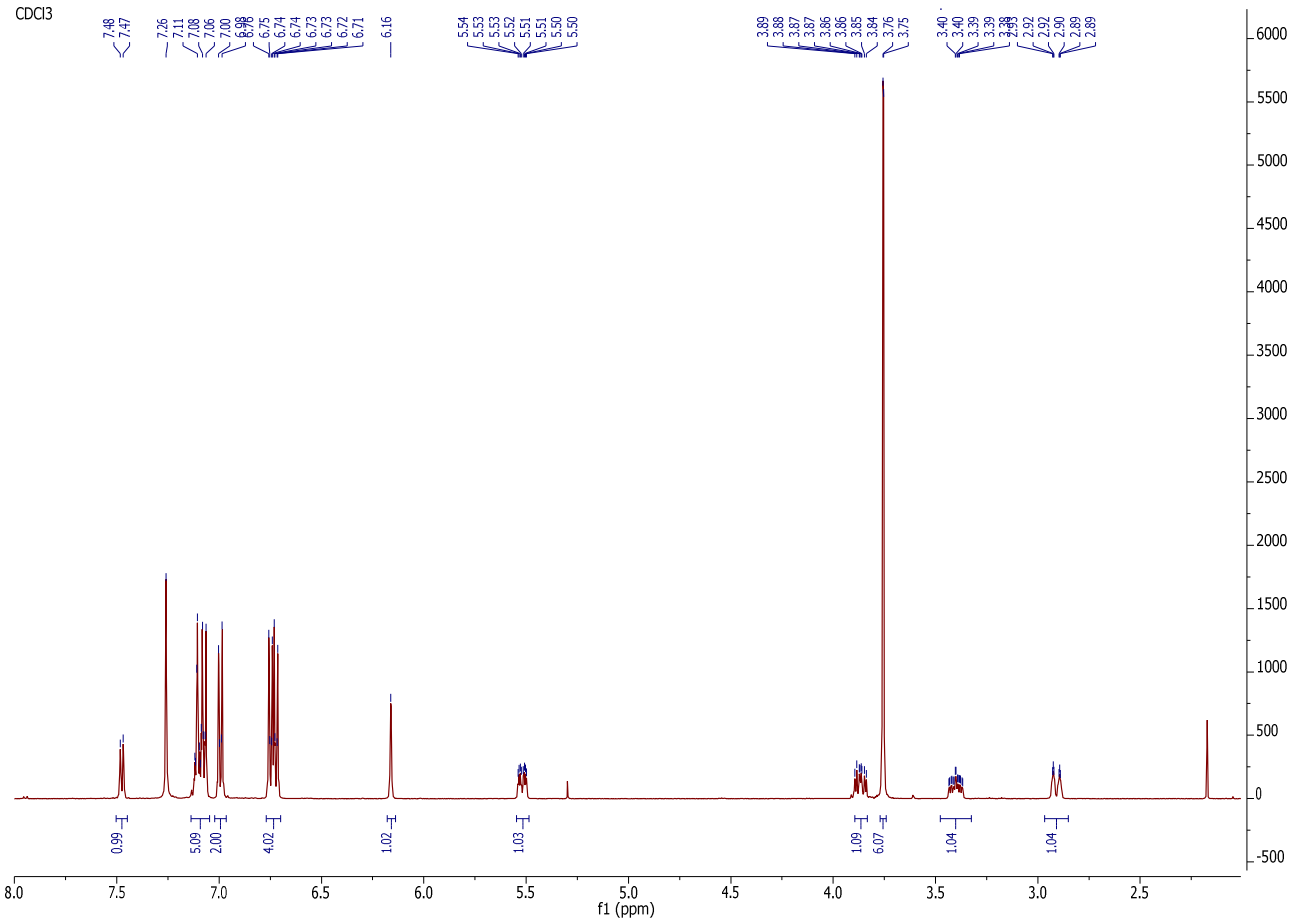

CDCl3
129.28
129.05
128.98
128.60
128.38
122.60
120.05
118.46
111.18
63.61
50.02
20.07
f1 (ppm)

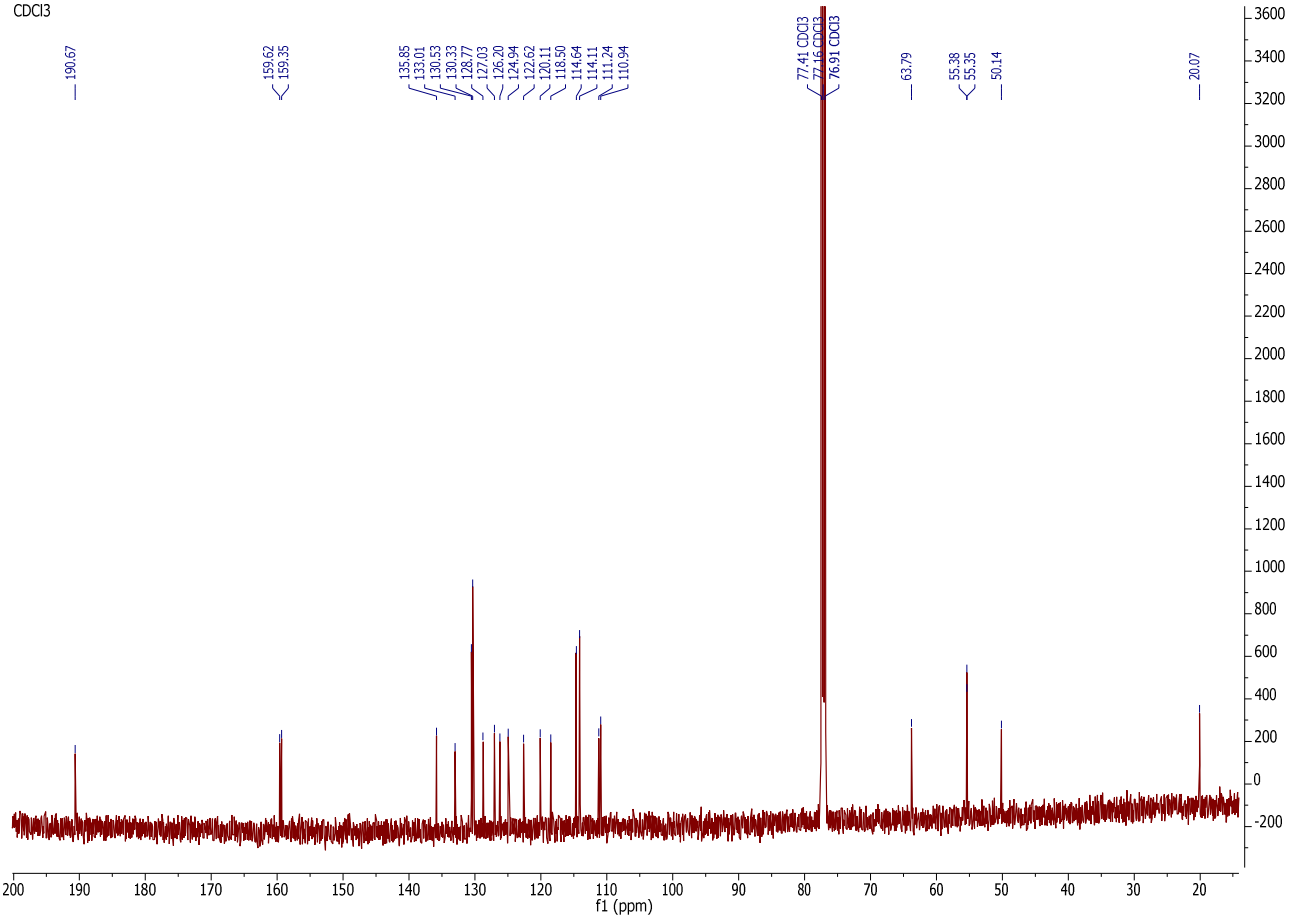

CDCl3
f2 (ppm)
f1 (ppm)

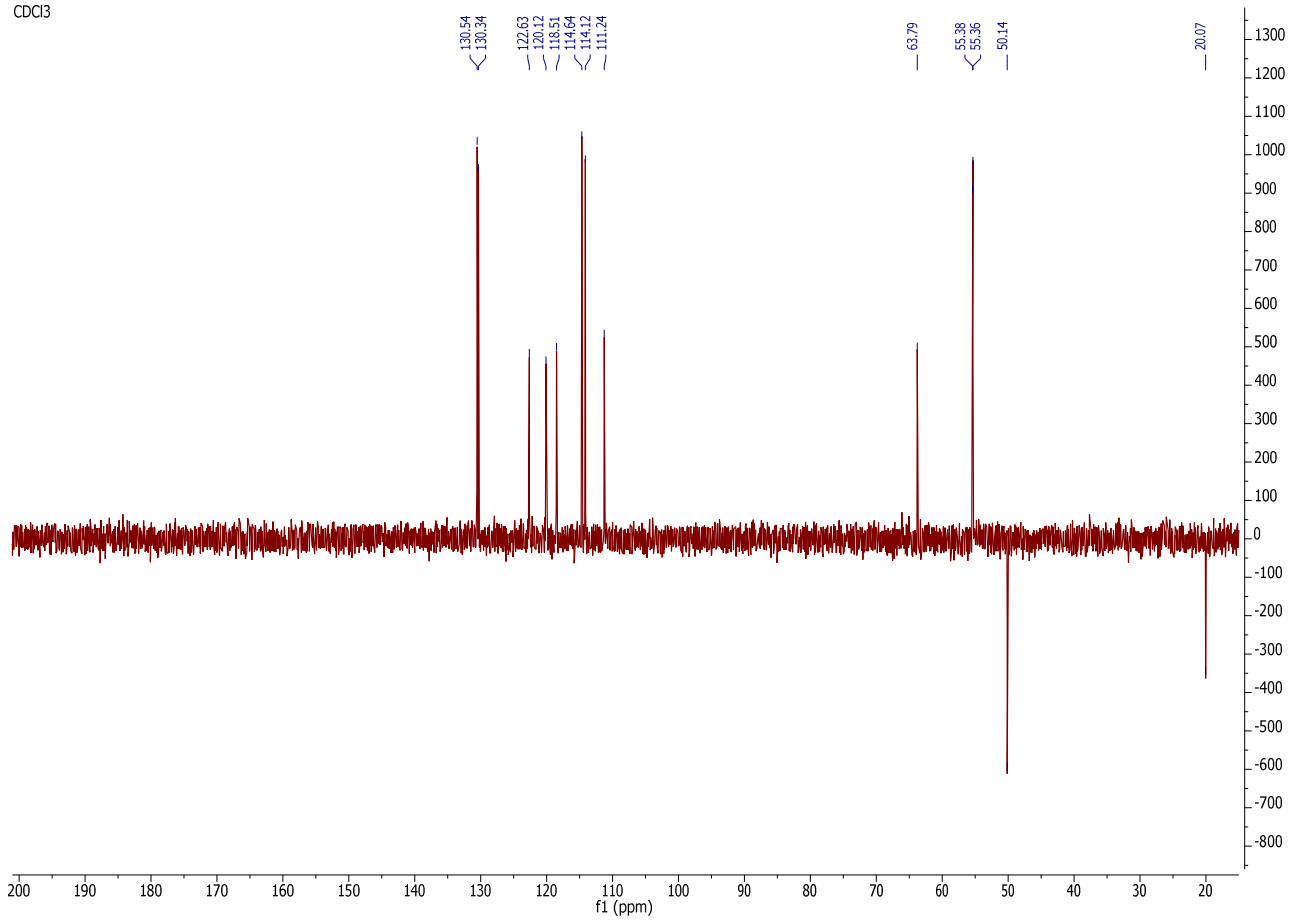

CDCl3
f2 (ppm)
f1 (ppm)

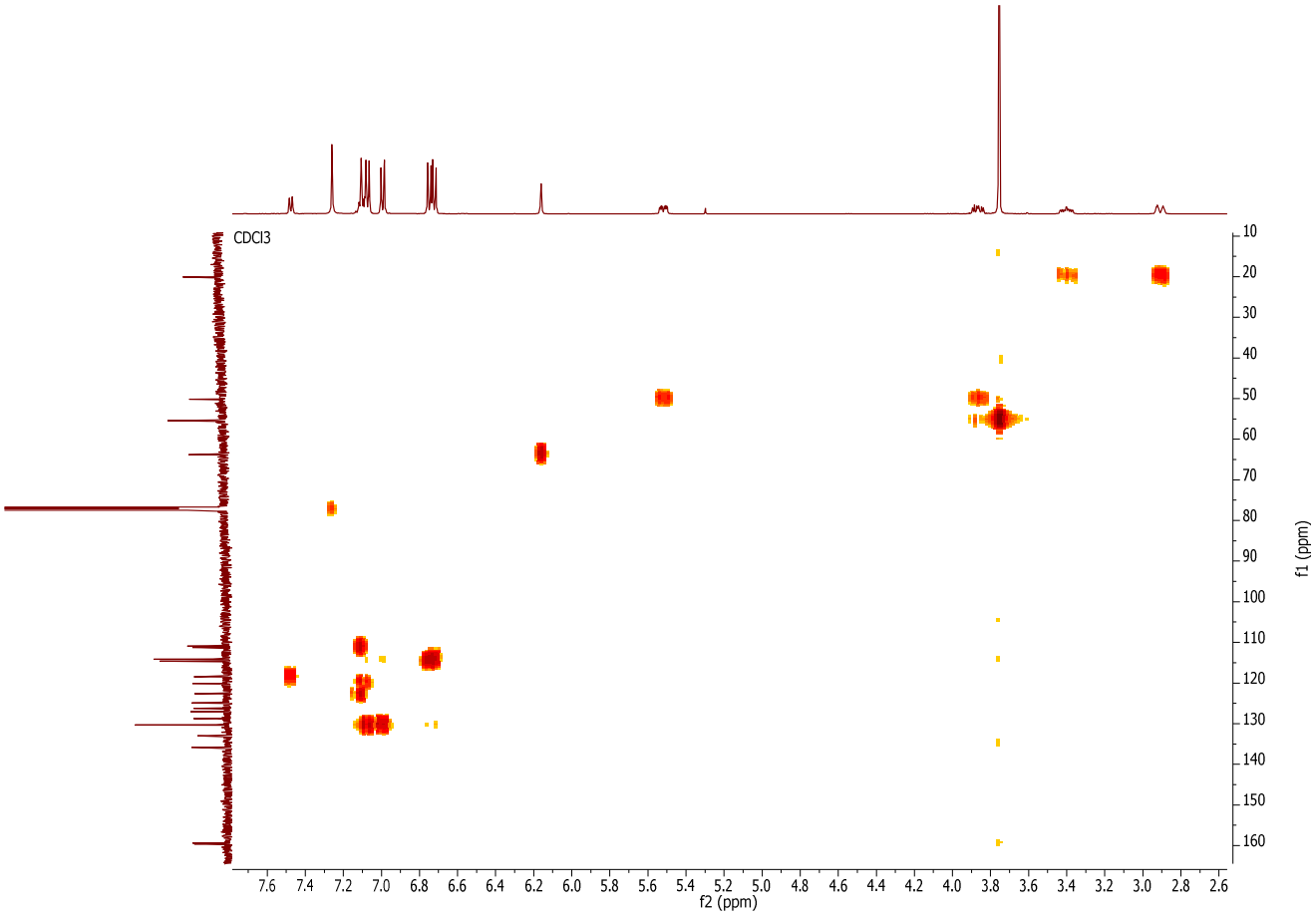


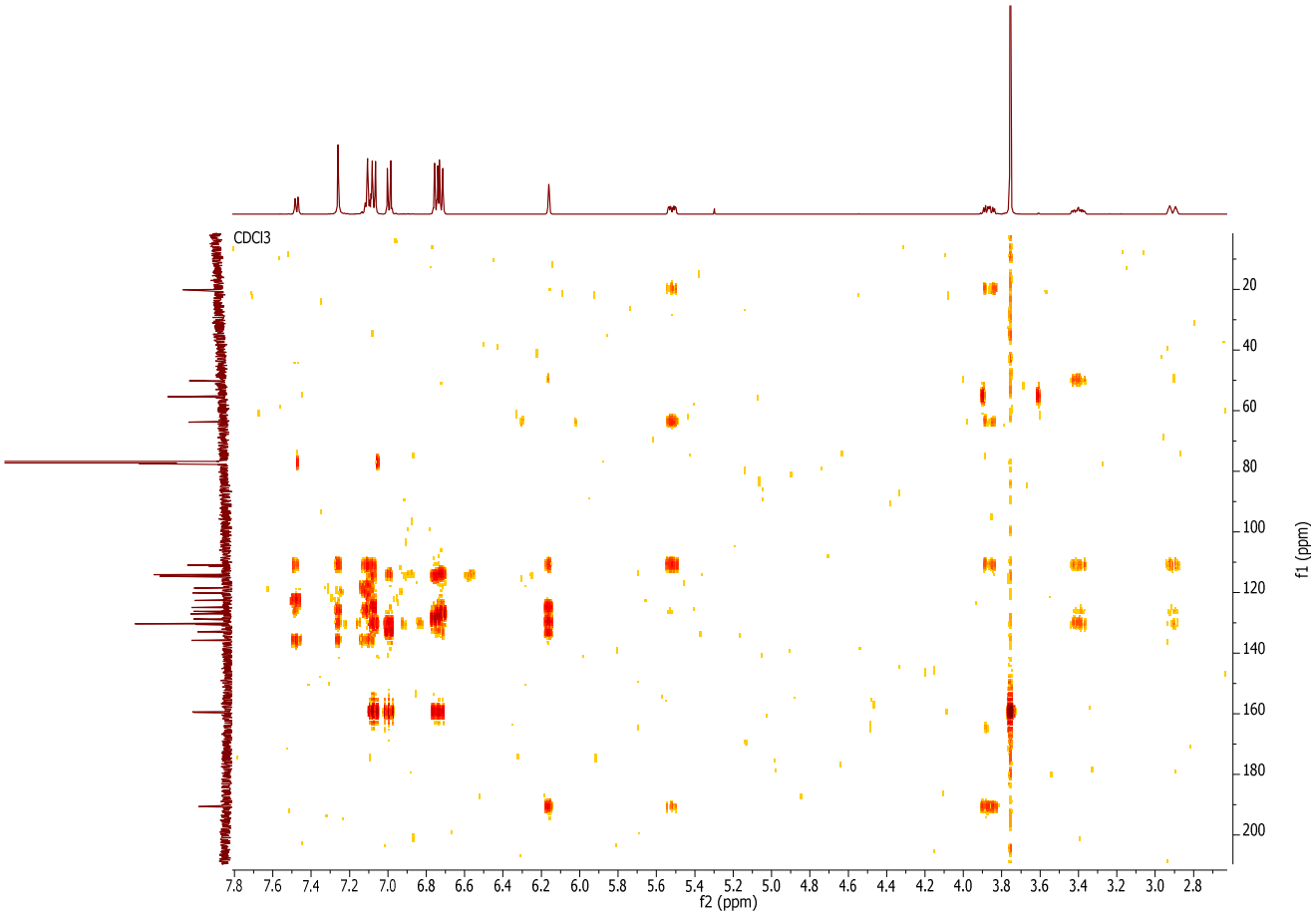
3b

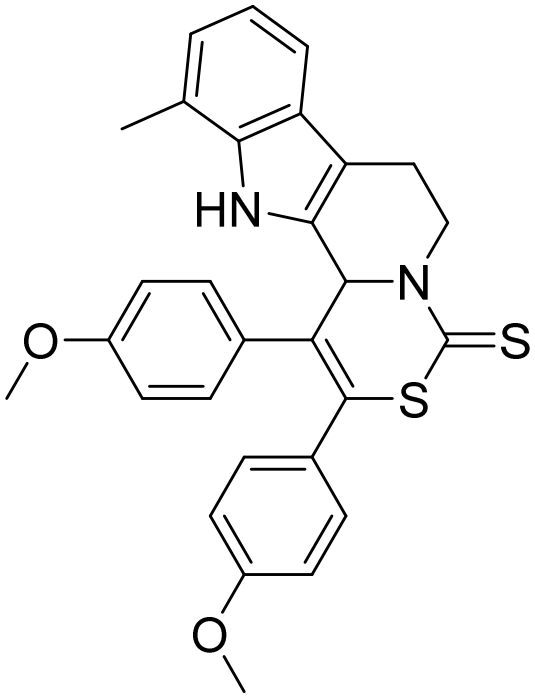



CDCl3
190.67
159.62
159.35
135.85
133.01
130.53
130.33
128.77
127.03
126.20
124.94
122.62
120.11
118.50
114.64
114.11
111.24
110.94
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
63.79
55.38
55.35
50.14
20.07
f1 (ppm)

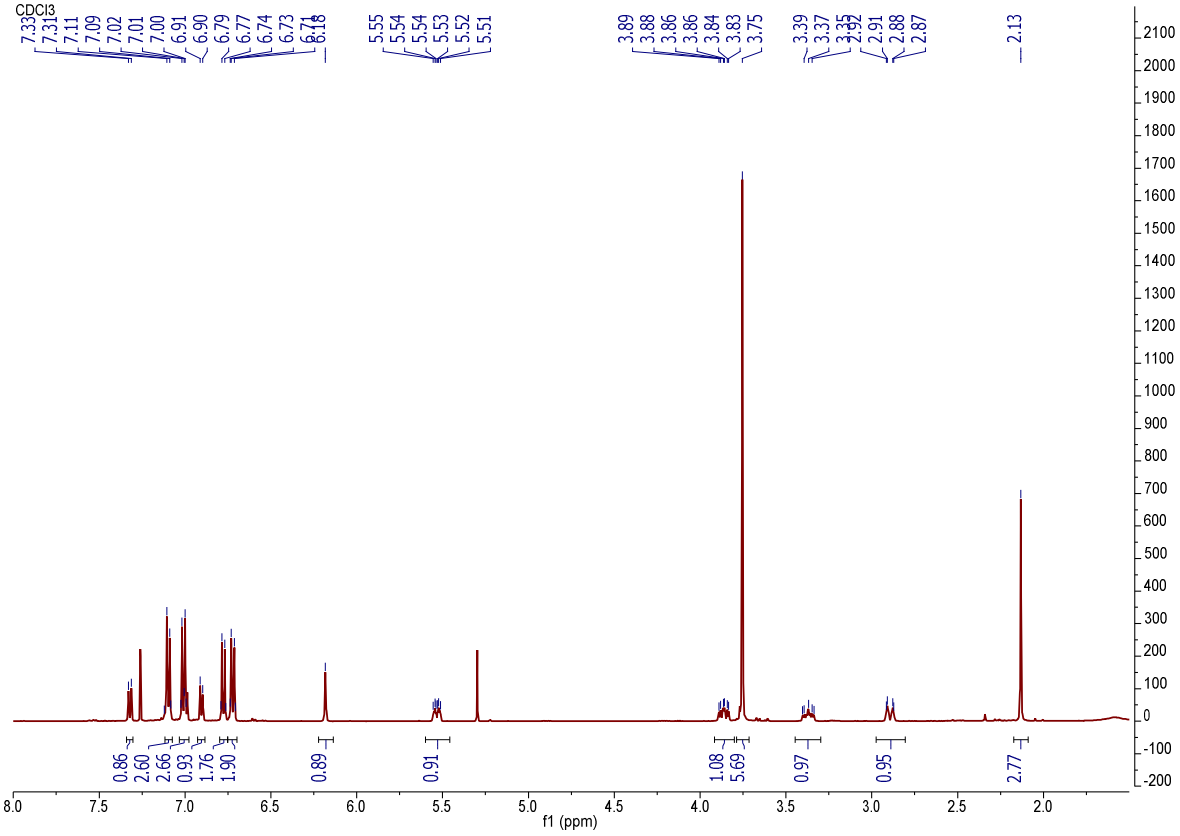

CDCl3
130.54
130.34
122.63
120.12
118.51
114.64
114.12
111.24
63.79
55.38
55.36
50.14
20.07
f1 (ppm)

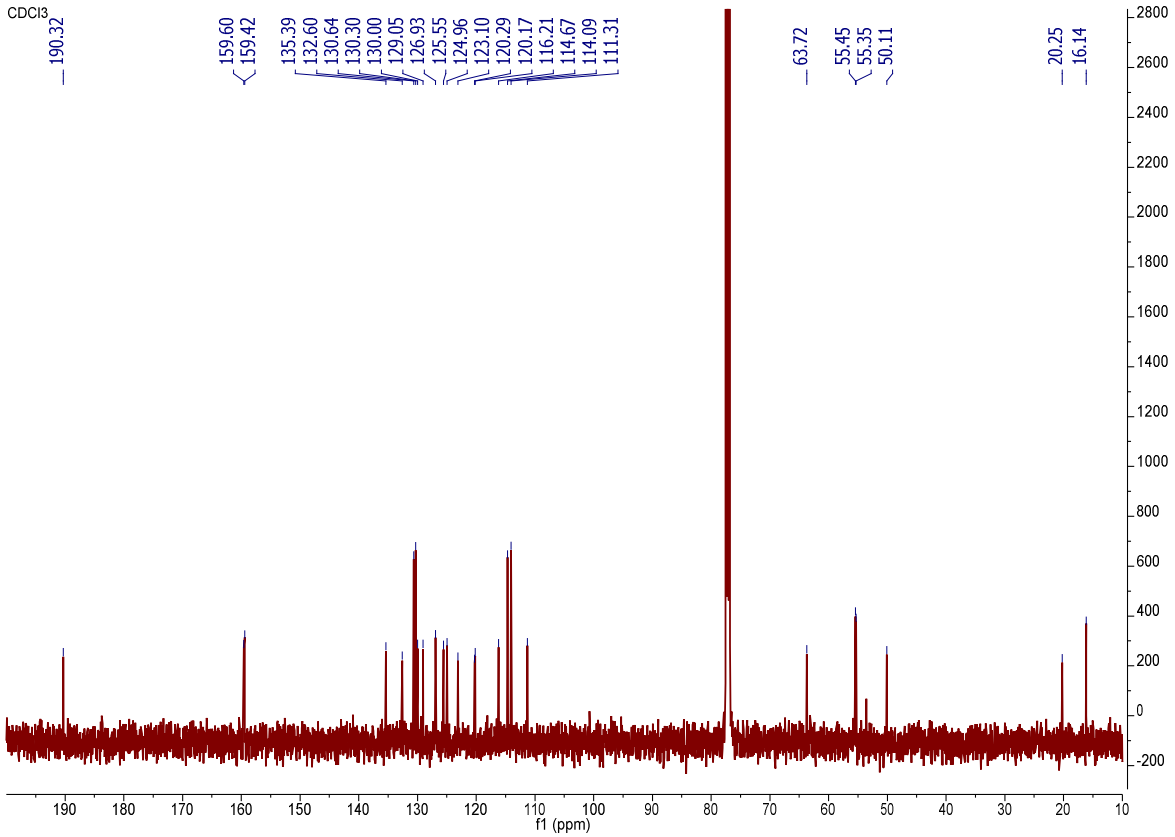

CDCl3
f2 (ppm)
f1 (ppm)

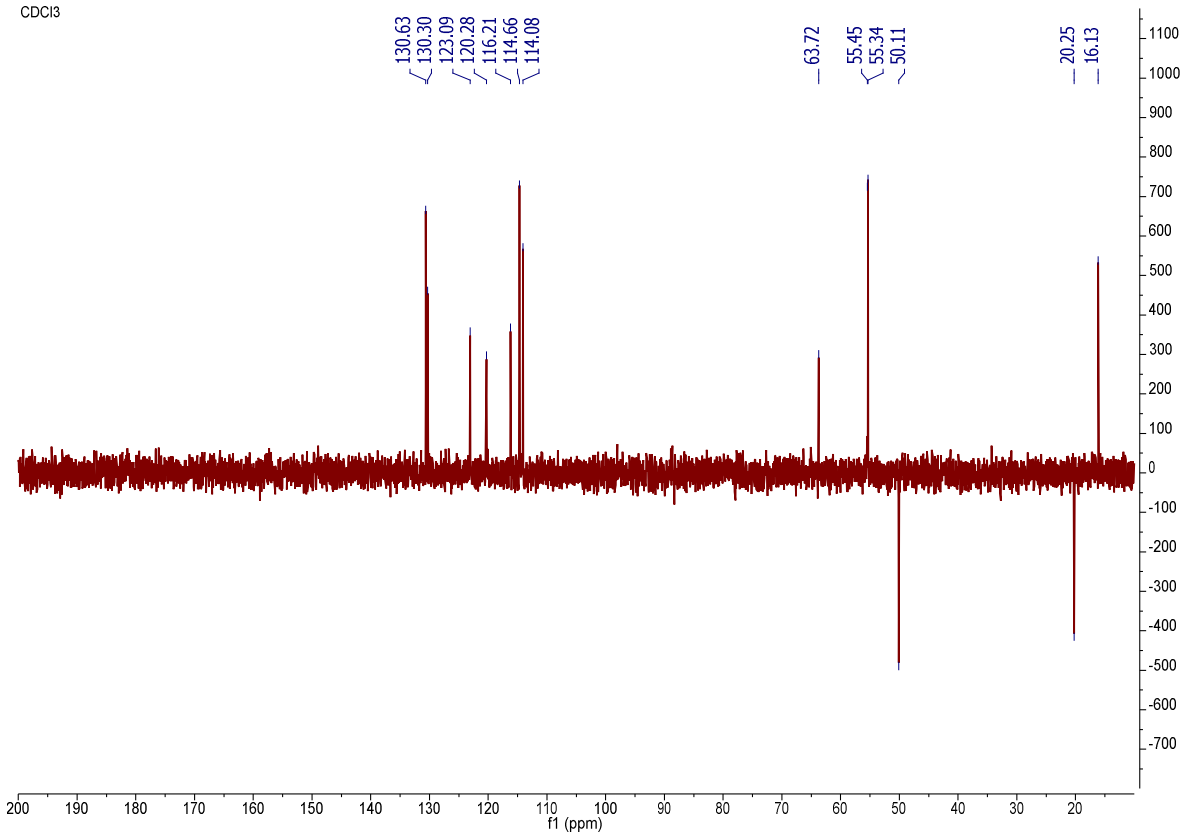

CDCl3
f2 (ppm)
f1 (ppm)

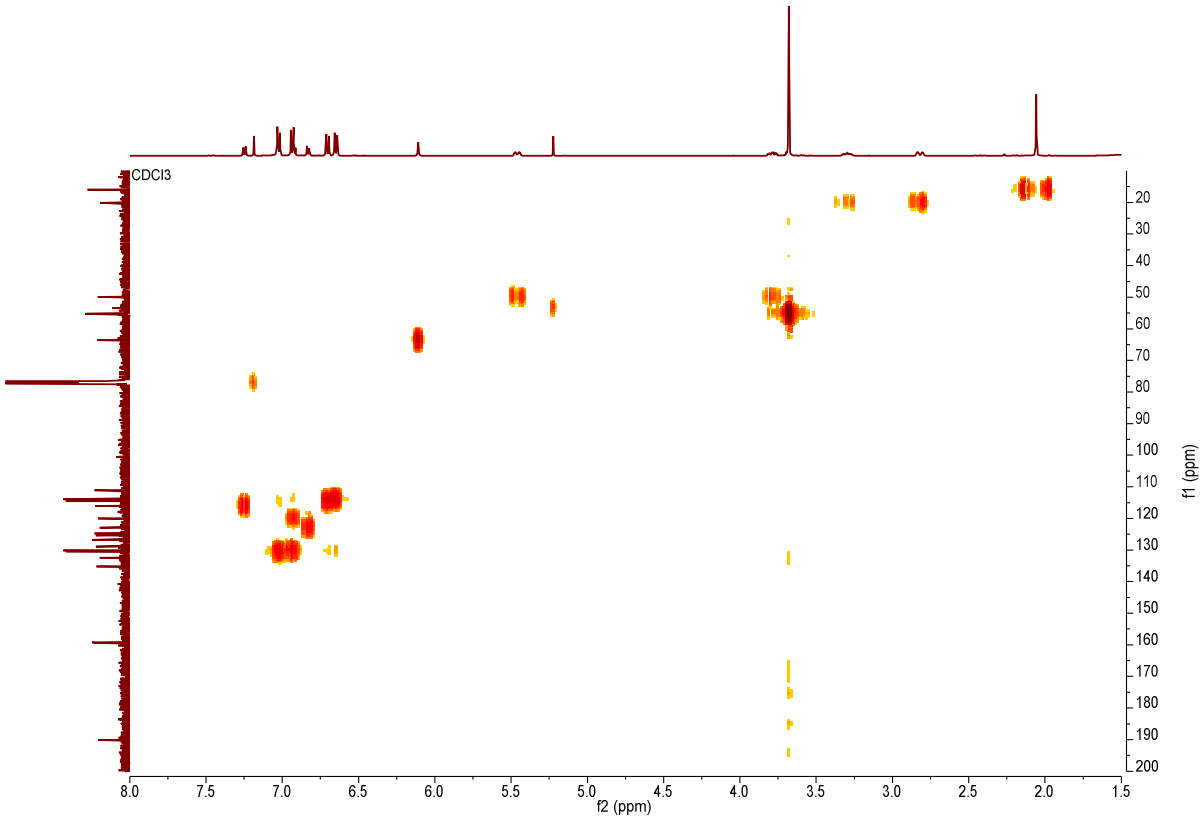

HN
N
O
S
S
O

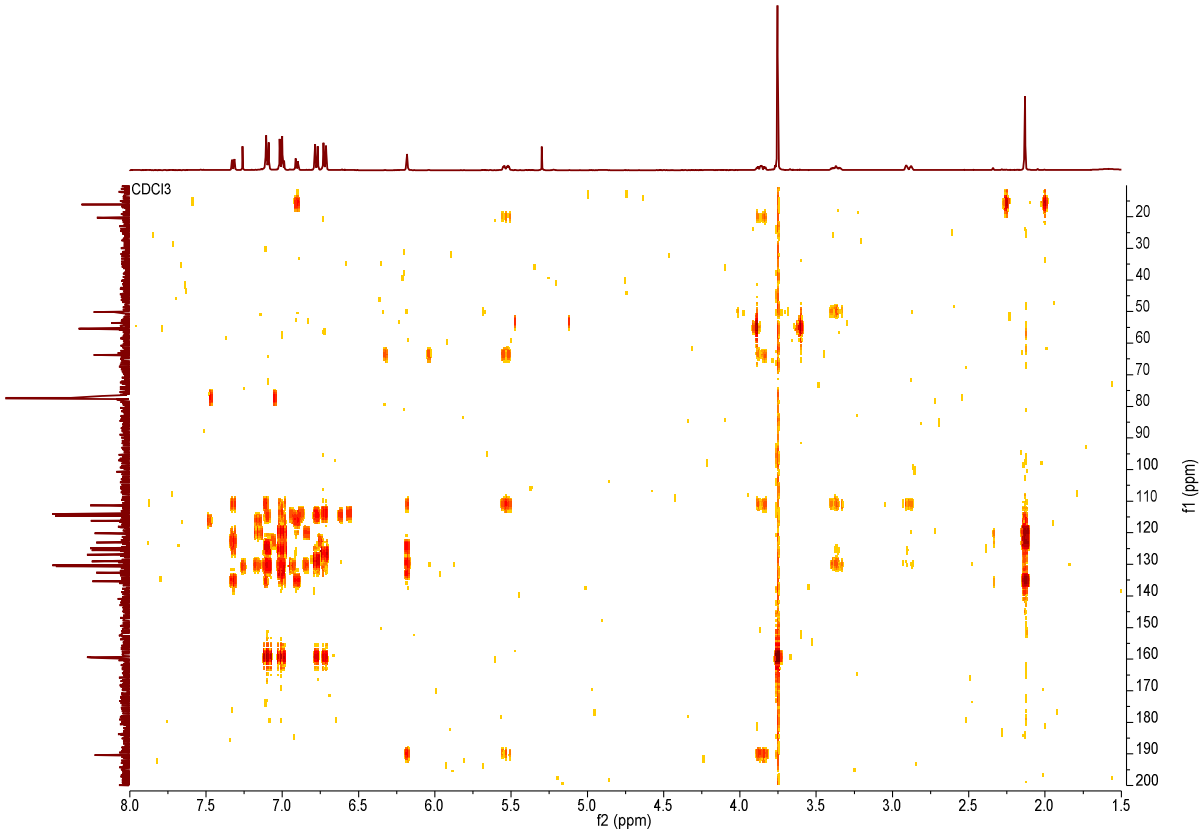
3c

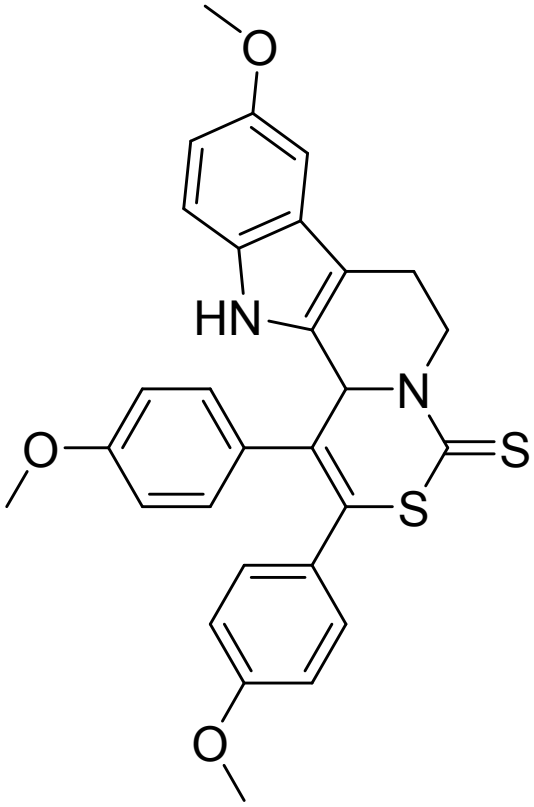

CDCl3
7.33
7.31
7.11
7.09
7.02
7.01
7.00
6.91
6.90
6.79
6.77
6.74
6.73
6.71
6.18
5.55
5.54
5.54
5.53
5.52
5.51
3.89
3.88
3.86
3.86
3.84
3.83
3.75
3.39
3.37
3.35
2.92
2.91
2.88
2.87
2.13
0.86
2.60
2.66
0.93
1.76
1.90
0.89
0.91
1.08
5.69
0.97
0.95
2.77
f1 (ppm)


CDCl3
190.32
159.60
159.42
135.39
132.60
130.64
130.30
130.00
129.05
126.93
125.55
124.96
123.10
120.29
120.17
116.21
114.67
114.09
111.31
63.72
55.45
55.35
50.11
20.25
16.14
f1 (ppm)

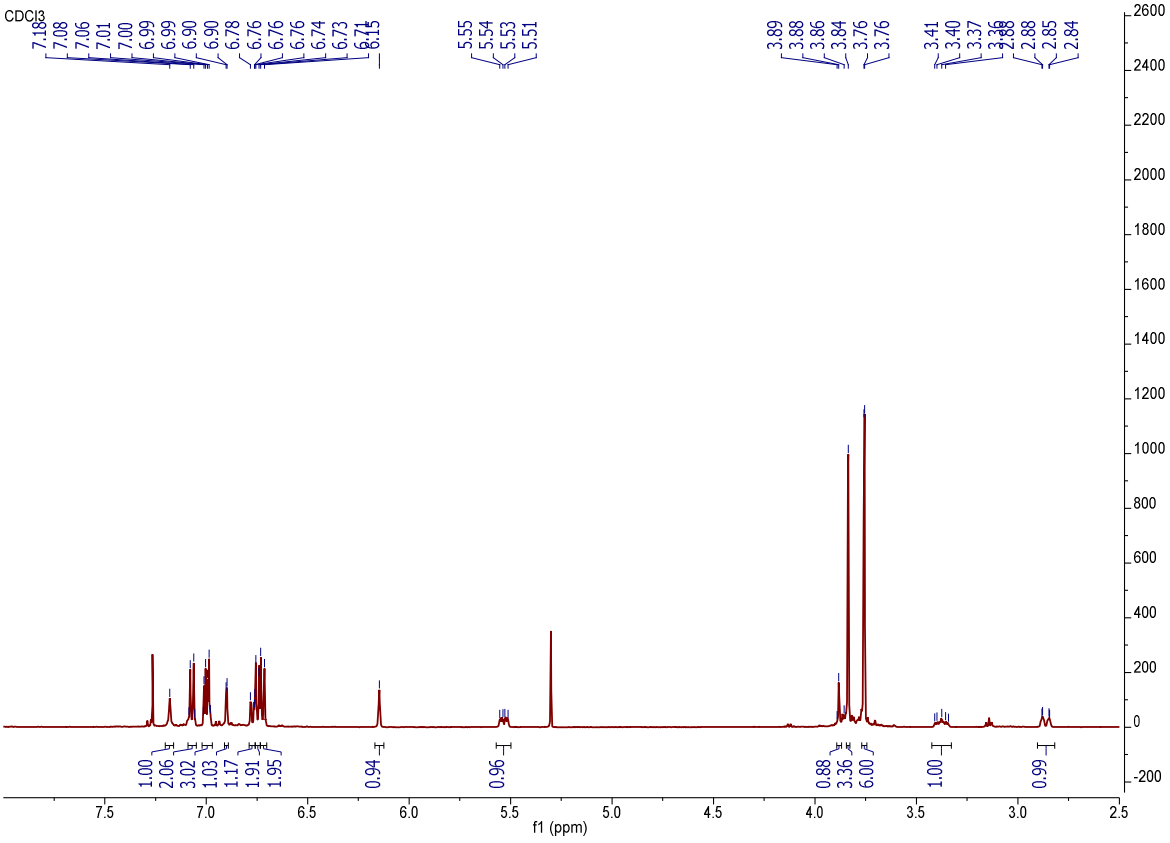

CDCl3
130.63
130.30
123.09
120.28
116.21
114.66
114.08
63.72
55.45
55.34
50.11
20.25
16.13
f1 (ppm)

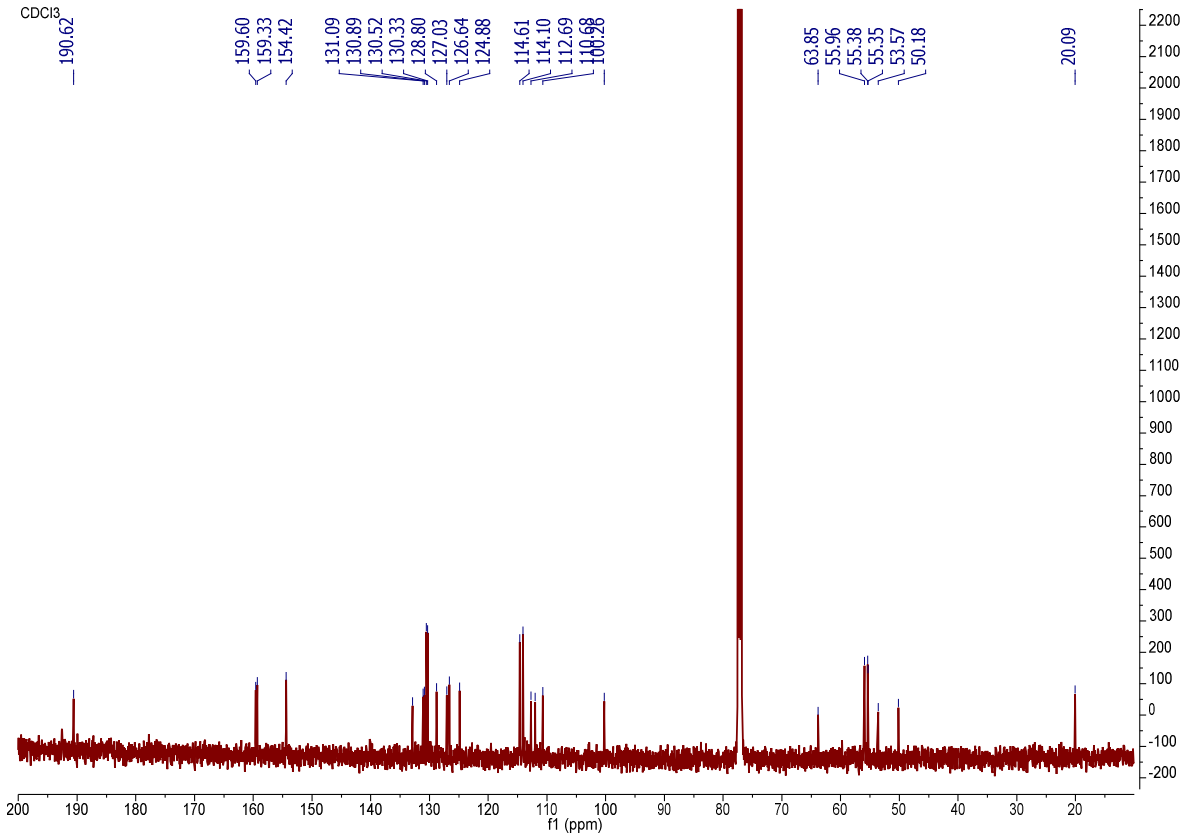

CDCl3
f2 (ppm)
f1 (ppm)


CDCl3
f2 (ppm)
f1 (ppm)


O
HN
N
O
S
S
O

3d


CDCl3
7.18
7.08
7.06
7.01
7.00
6.99
6.99
6.90
6.90
6.78
6.76
6.76
6.76
6.74
6.73
6.71
6.15
5.55
5.54
5.53
5.51
3.89
3.88
3.86
3.84
3.76
3.76
3.41
3.40
3.37
2.88
2.85
2.84
1.00
2.06
3.02
1.03
1.17
1.91
1.95
0.94
0.96
0.88
3.36
6.00
1.00
0.99
f1 (ppm)


CDCl3
190.62
159.60
159.33
154.42
131.09
130.89
130.52
130.33
128.80
127.03
126.64
124.88
114.61
114.10
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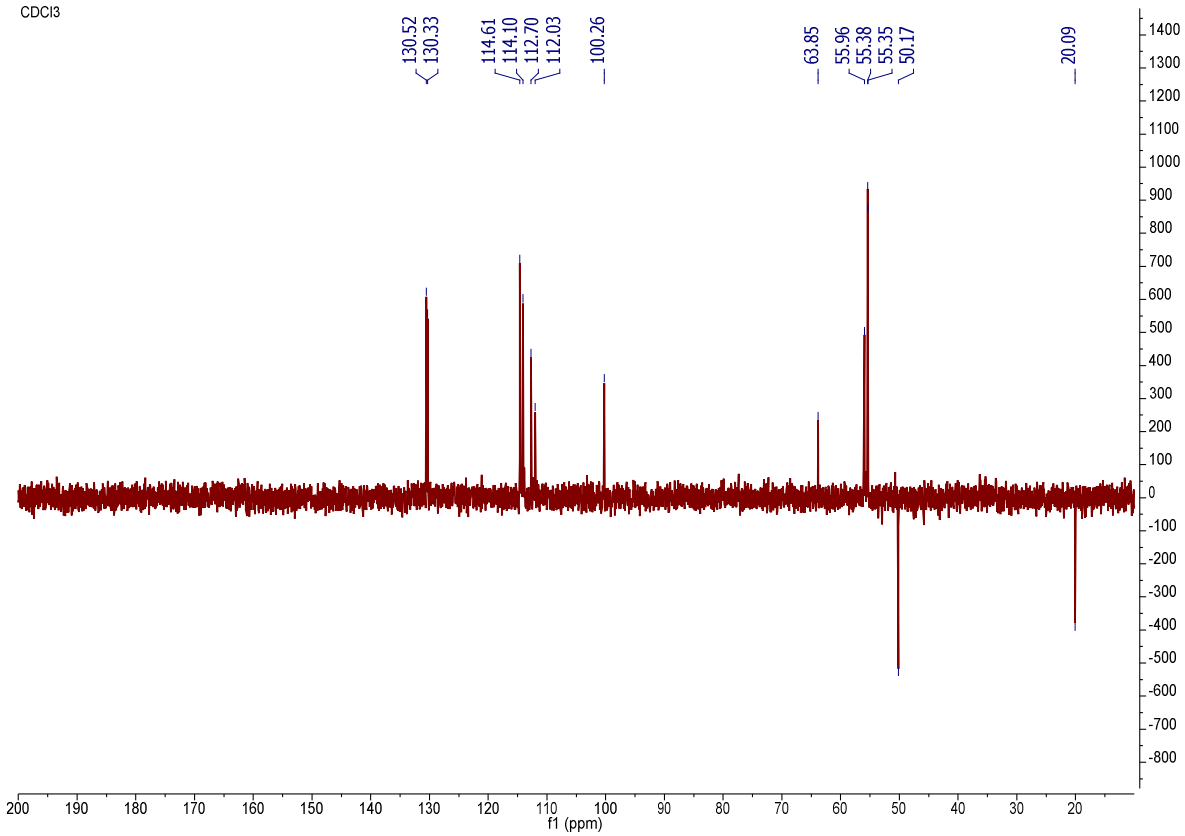
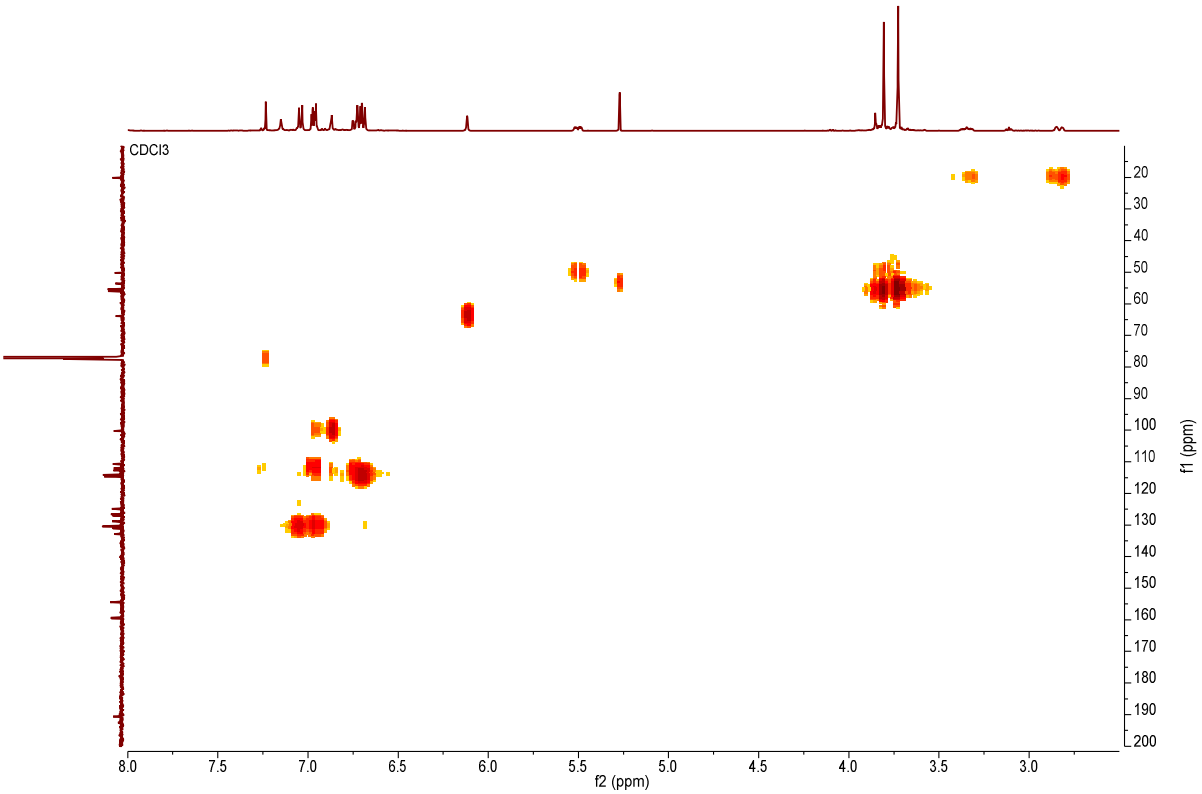
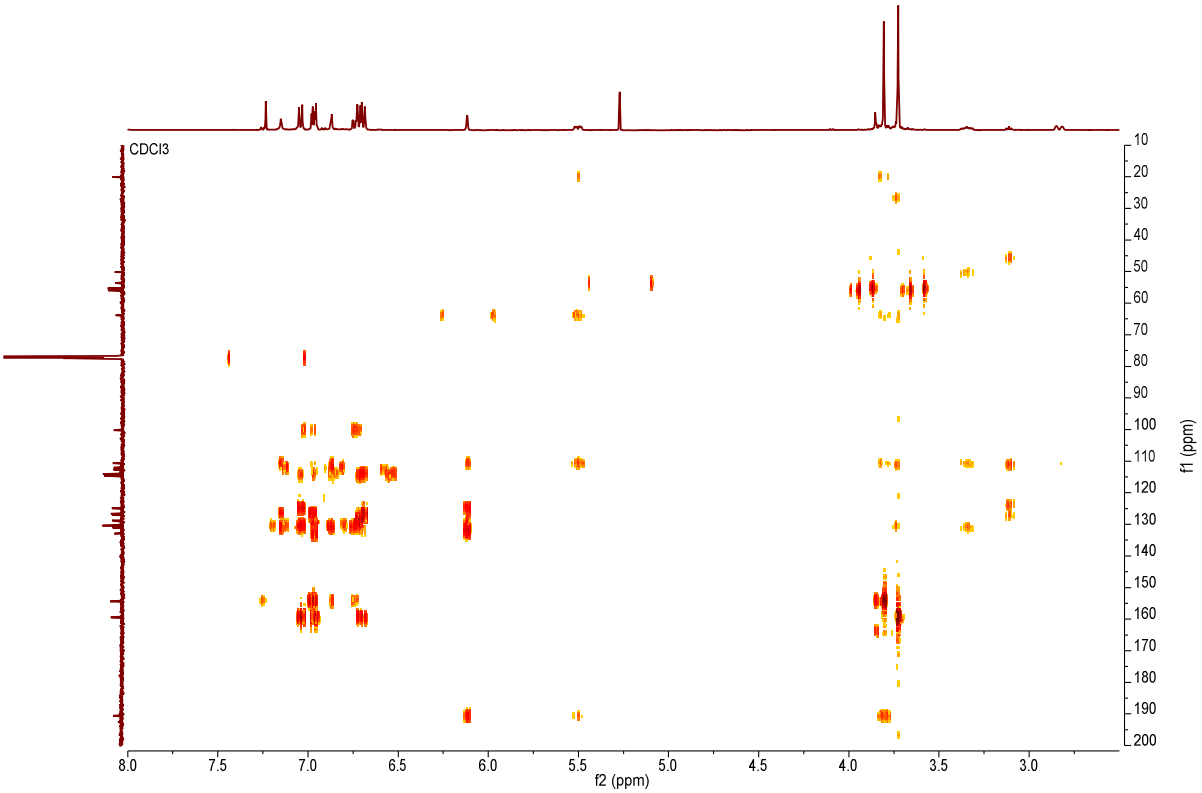
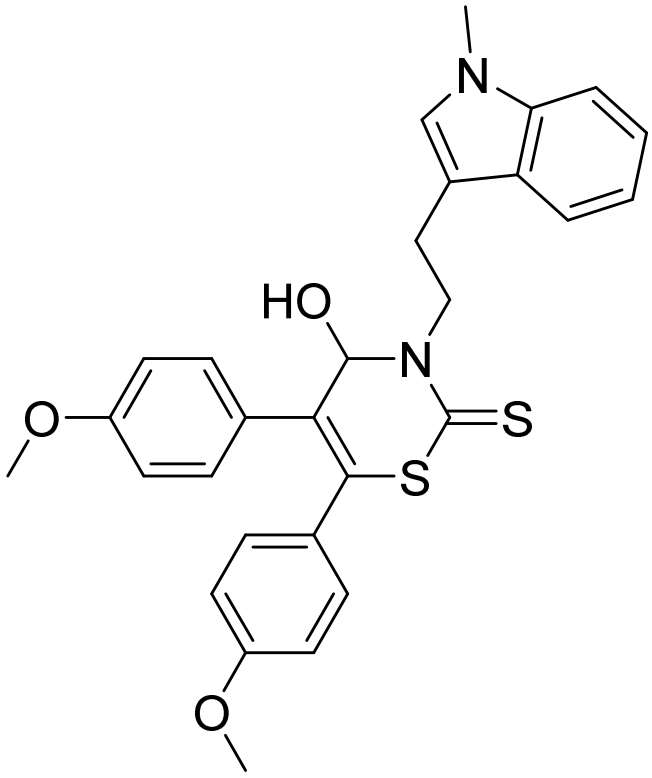
55.38
55.35
53.57
50.18
20.09
f1 (ppm)

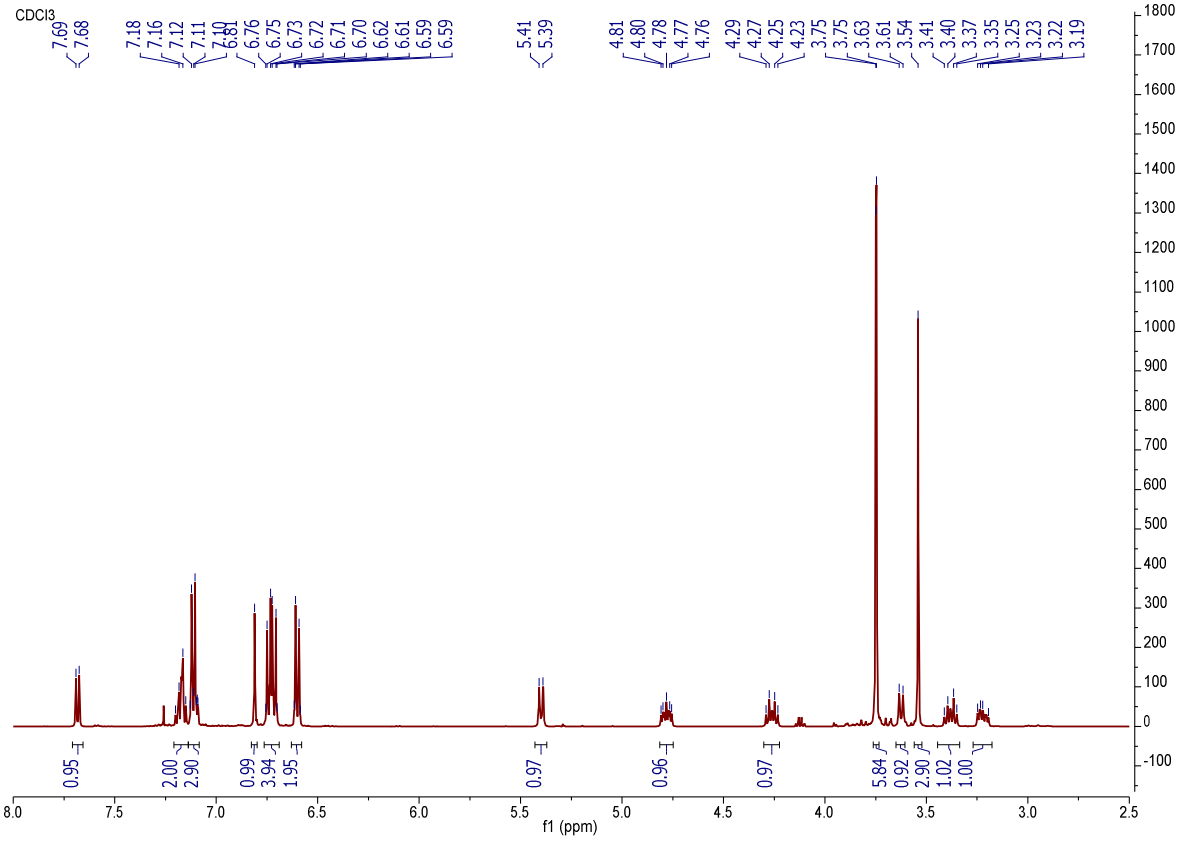

CDCl3
130.52
130.33
114.61
114.10
112.70
112.03
100.26
63.85
55.96
55.38
55.35
50.17
20.09
f1 (ppm)

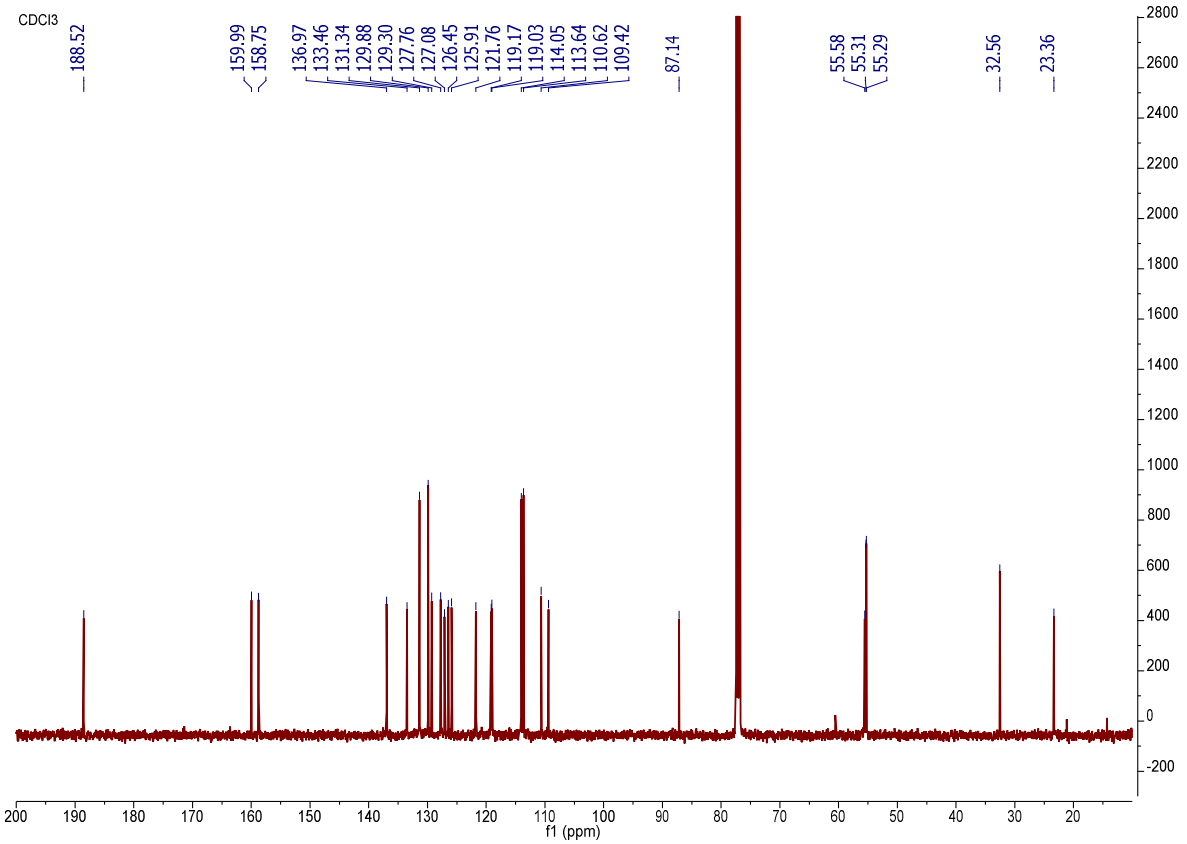

CDCl3
f2 (ppm)
f1 (ppm)

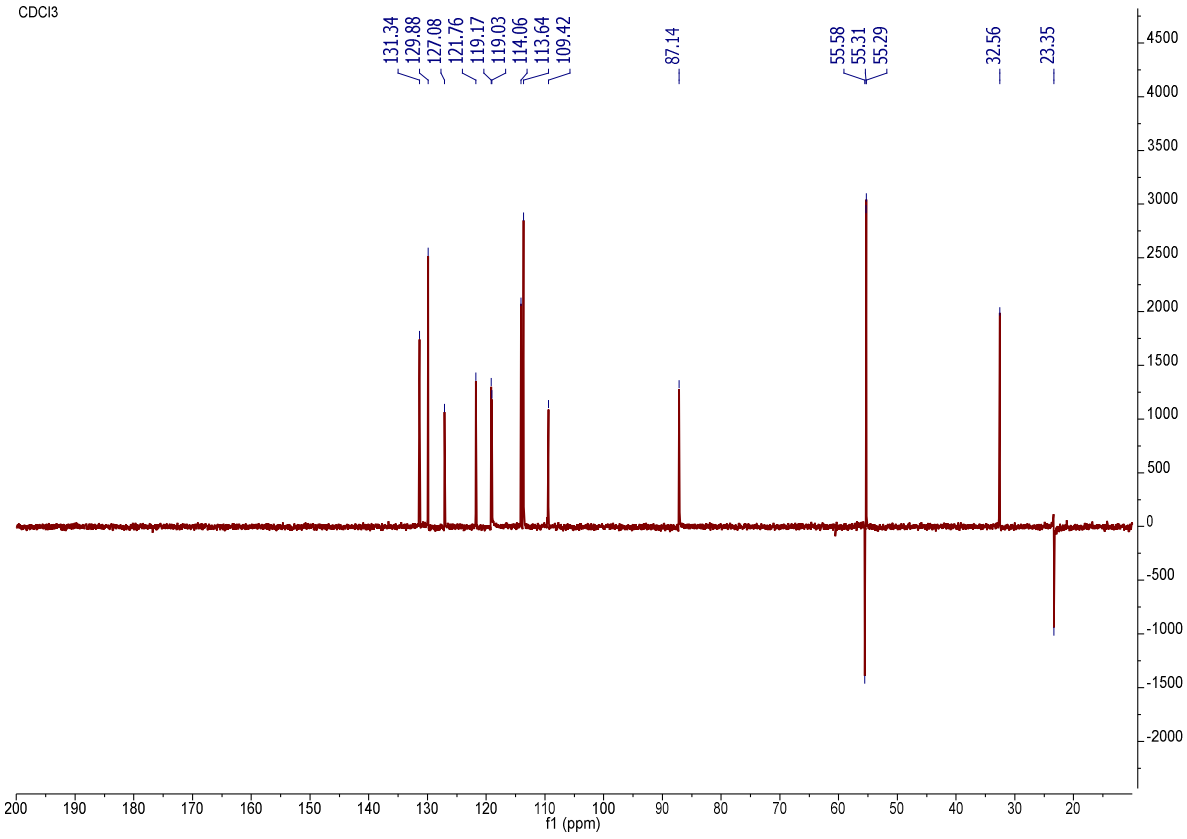

CDCl3
f2 (ppm)
f1 (ppm)

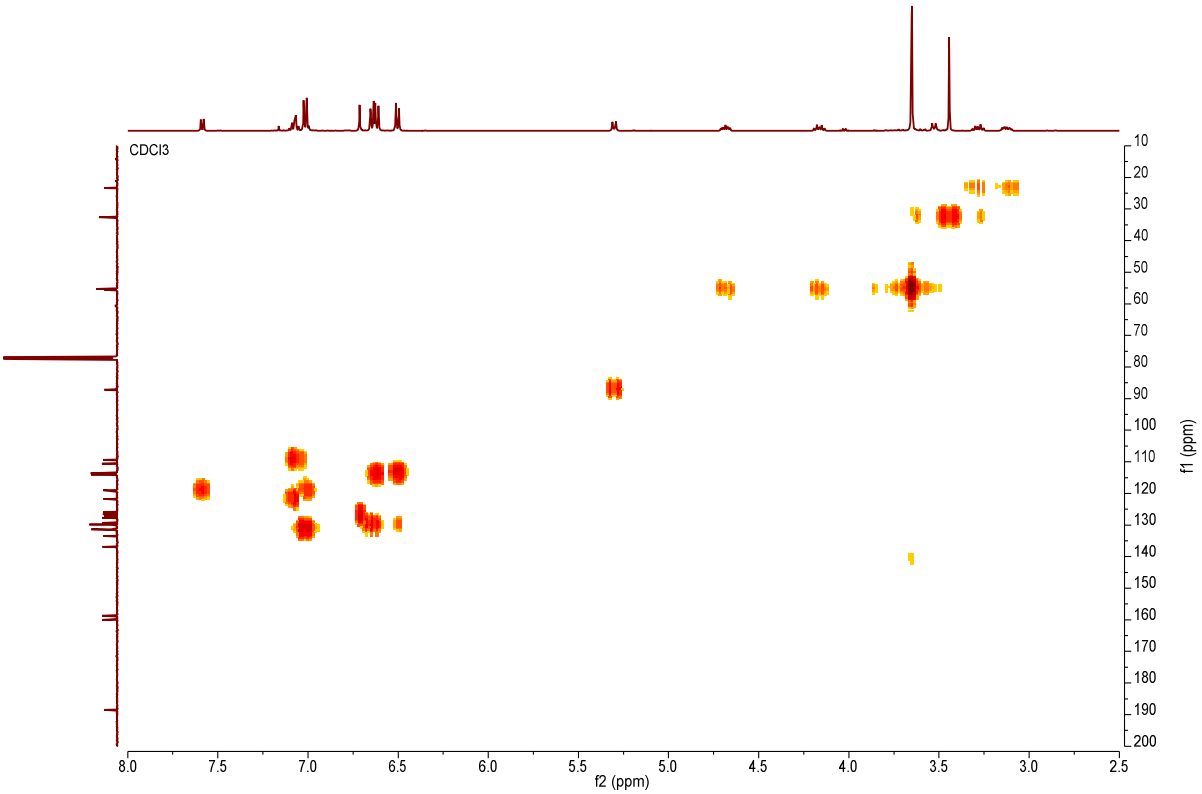


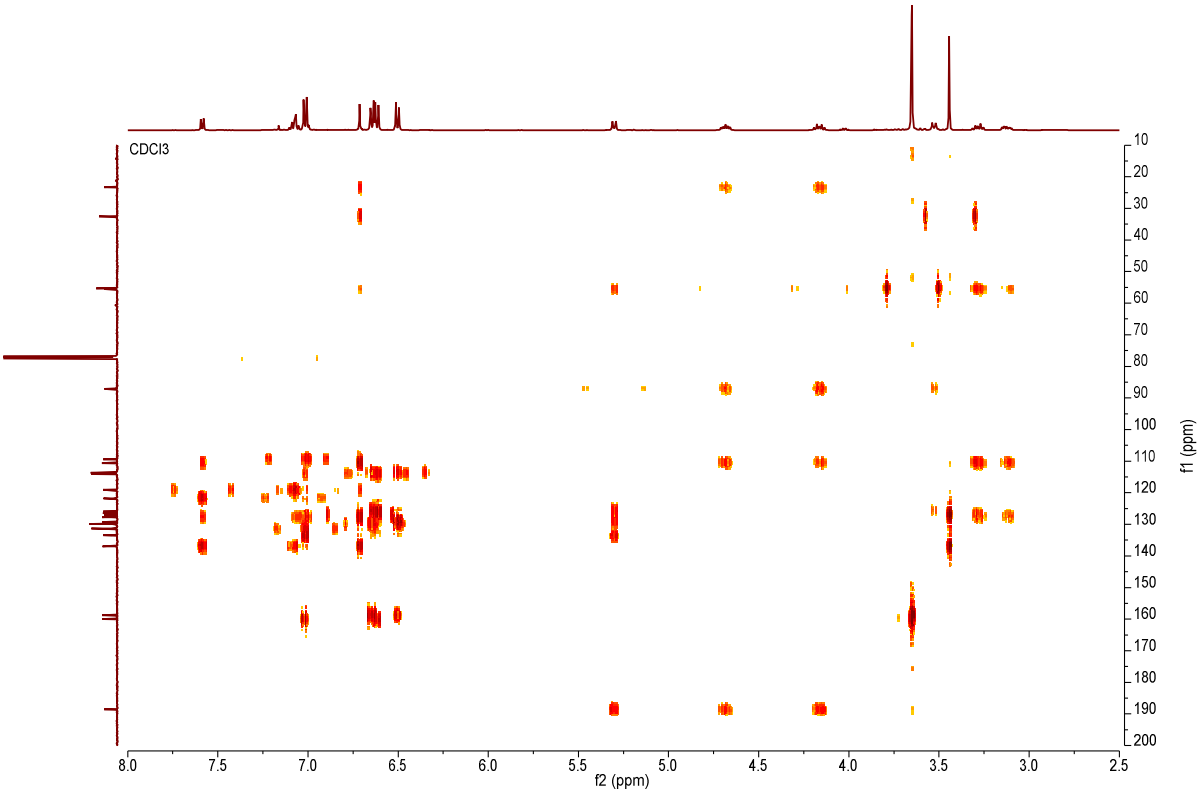
2x

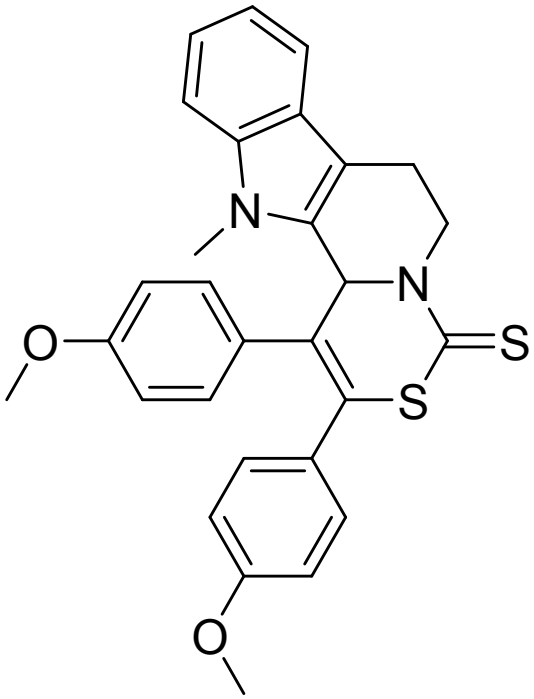



CDCl3
188.52
159.99
158.75
136.97
133.46
131.34
129.88
129.30
127.76
127.08
126.45
125.91
121.76
119.17
119.03
114.05
113.64
110.62
109.42
87.14
55.58
55.31
55.29
32.56
23.36
f1 (ppm)

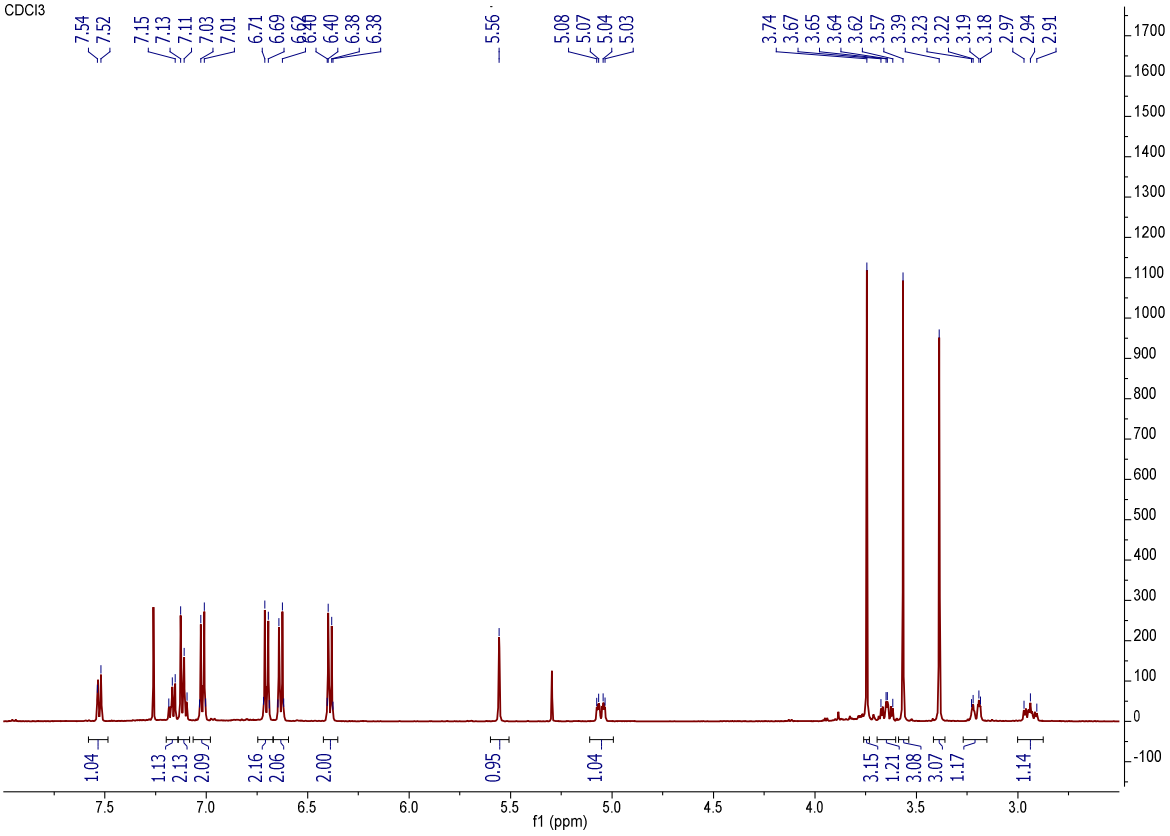

CDCl3
131.34
129.88
127.08
121.76
119.17
119.03
114.06
113.64
109.42
87.14
55.58
55.31
55.29
32.56
23.35
f1 (ppm)

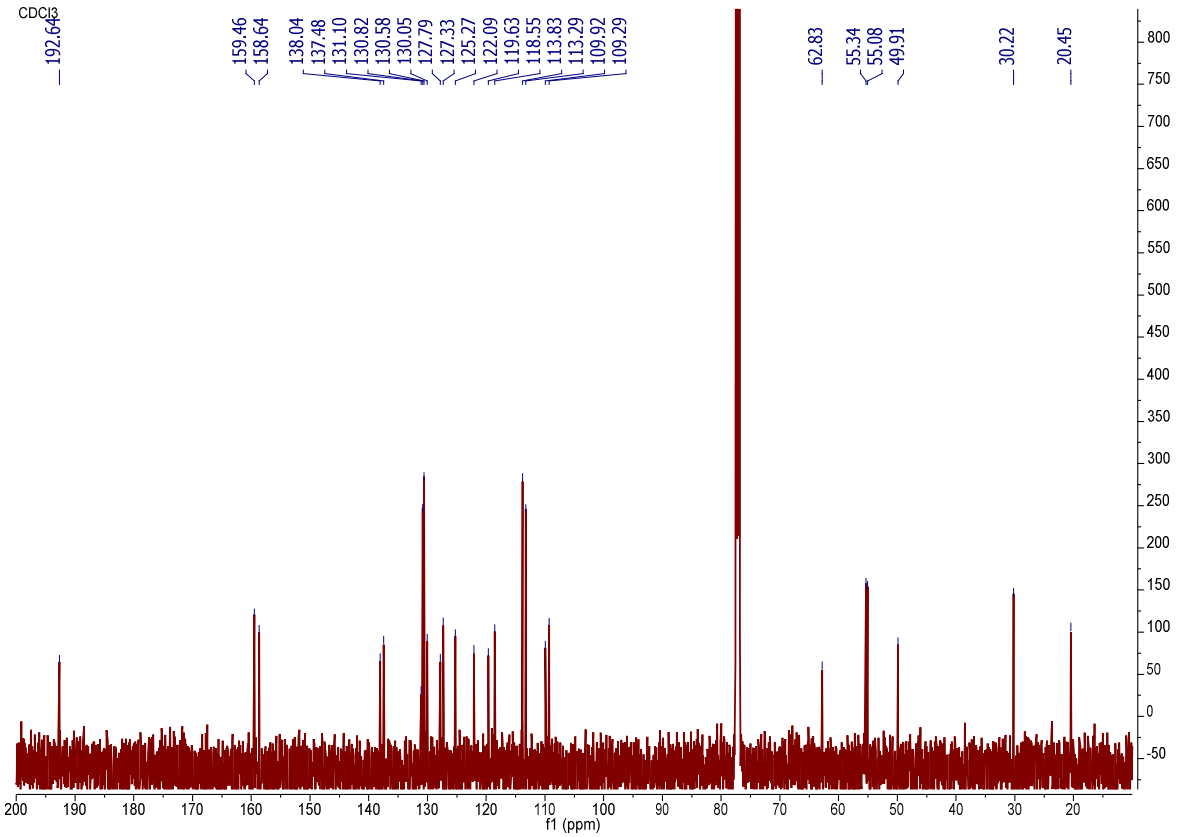

CDCl3
f2 (ppm)
f1 (ppm)

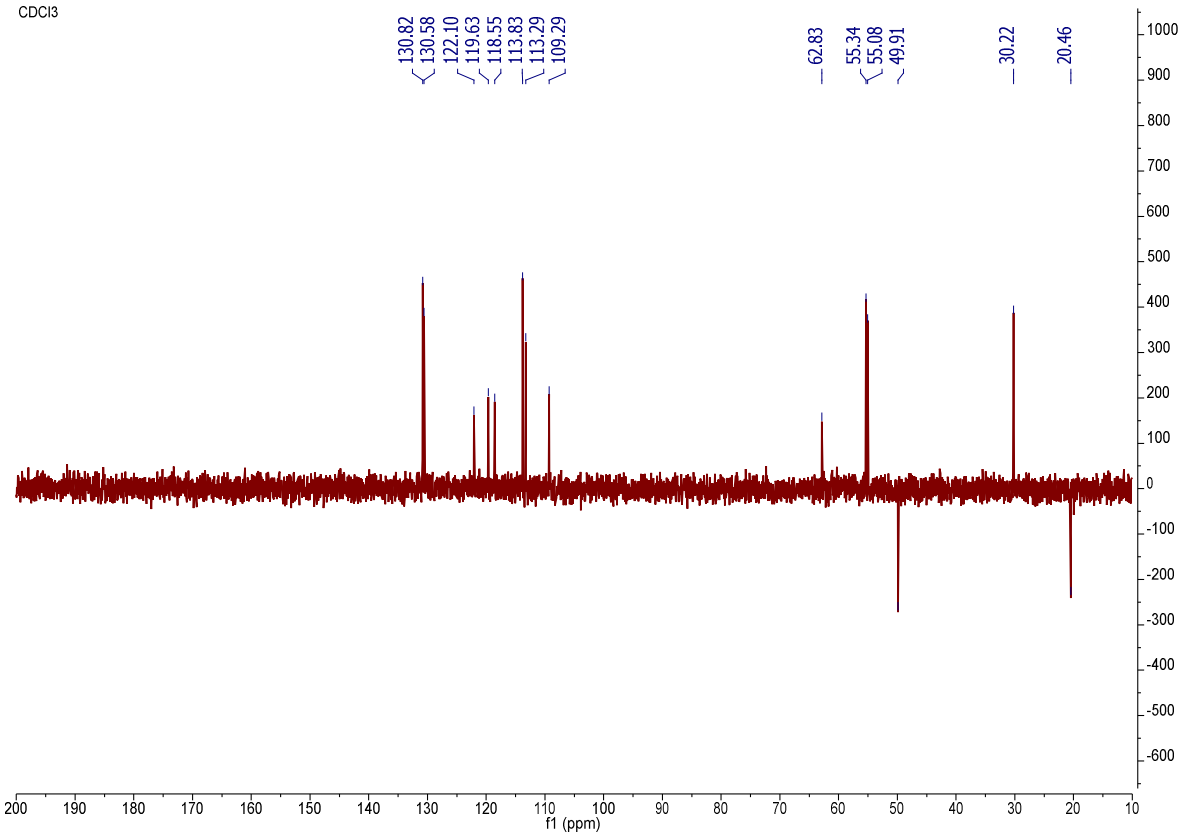

CDCl3
f2 (ppm)
f1 (ppm)

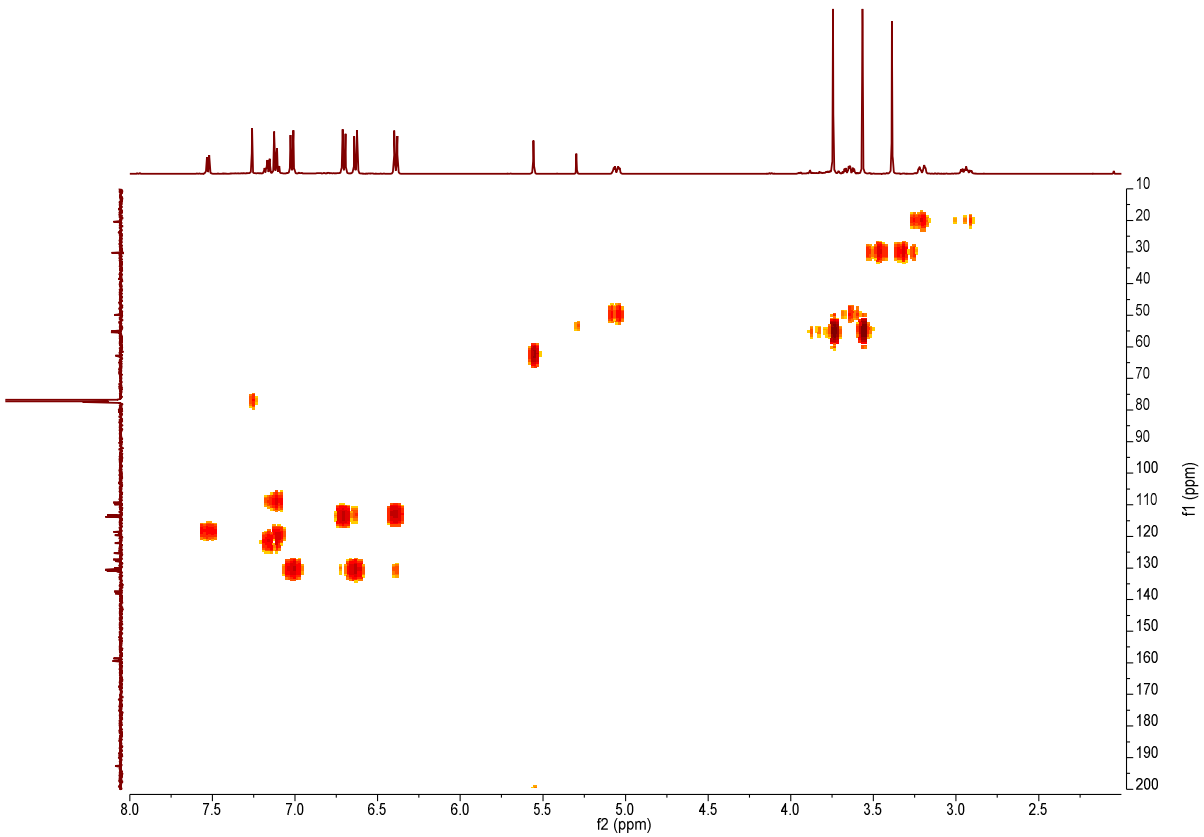

N
N
O
S
S
O

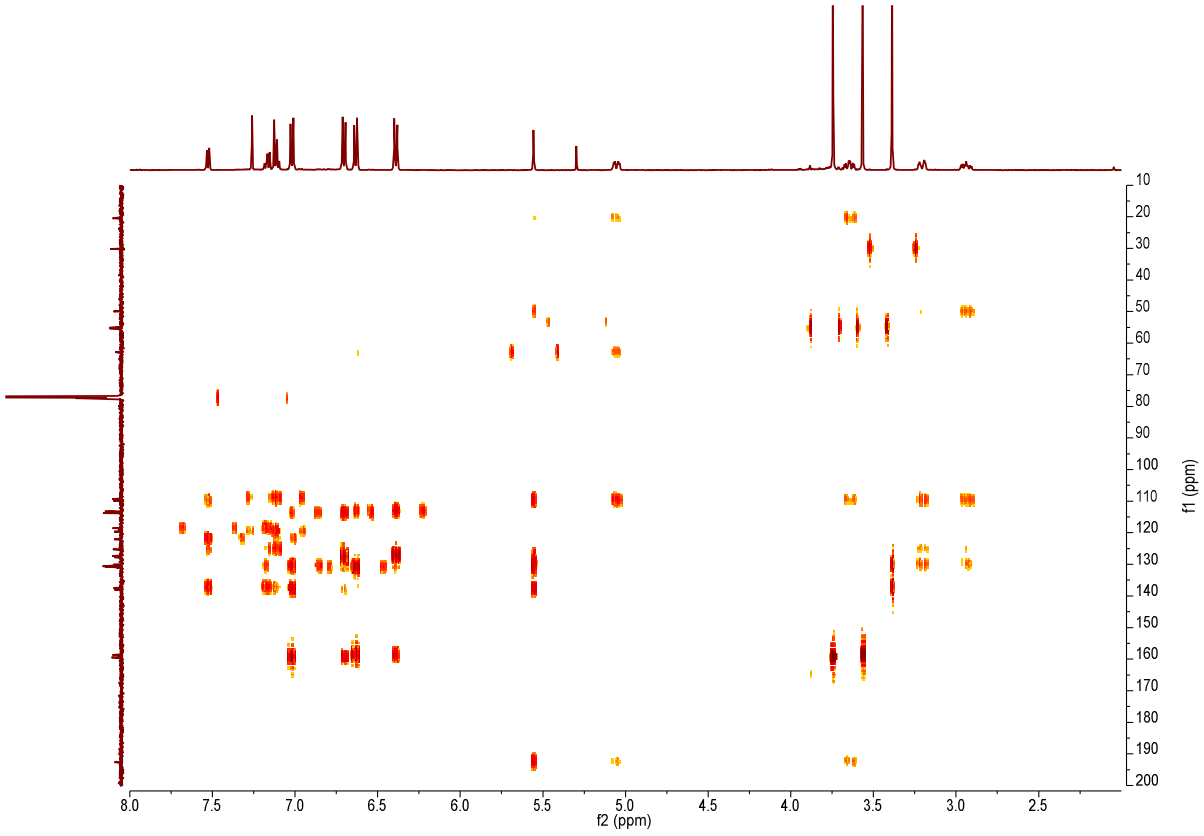
3e

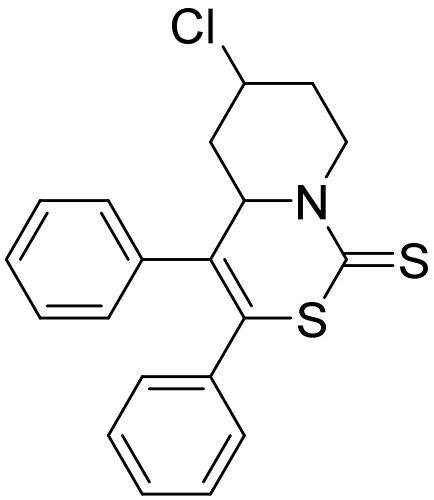

CDCl3
7.54
7.52
7.15
7.13
7.11
7.03
7.01
6.71
6.69
6.40
6.38
6.38
5.56
5.08
5.07
5.04
5.03
3.74
3.67
3.65
3.64
3.62
3.57
3.39
3.23
3.22
3.19
3.18
2.97
2.94
2.91
1.04
1.13
2.13
2.09
2.16
2.06
2.00
0.95
1.04
3.15
1.21
3.08
3.07
1.17
1.14
f1 (ppm)


CDCl3
192.64
159.46
158.64
138.04
137.48
131.10
130.82
130.58
130.05
127.79
127.33
125.27
122.09
119.63
118.55
113.83
113.29
109.92
109.29
62.83
55.34
55.08
49.91
30.22
20.45
f1 (ppm)

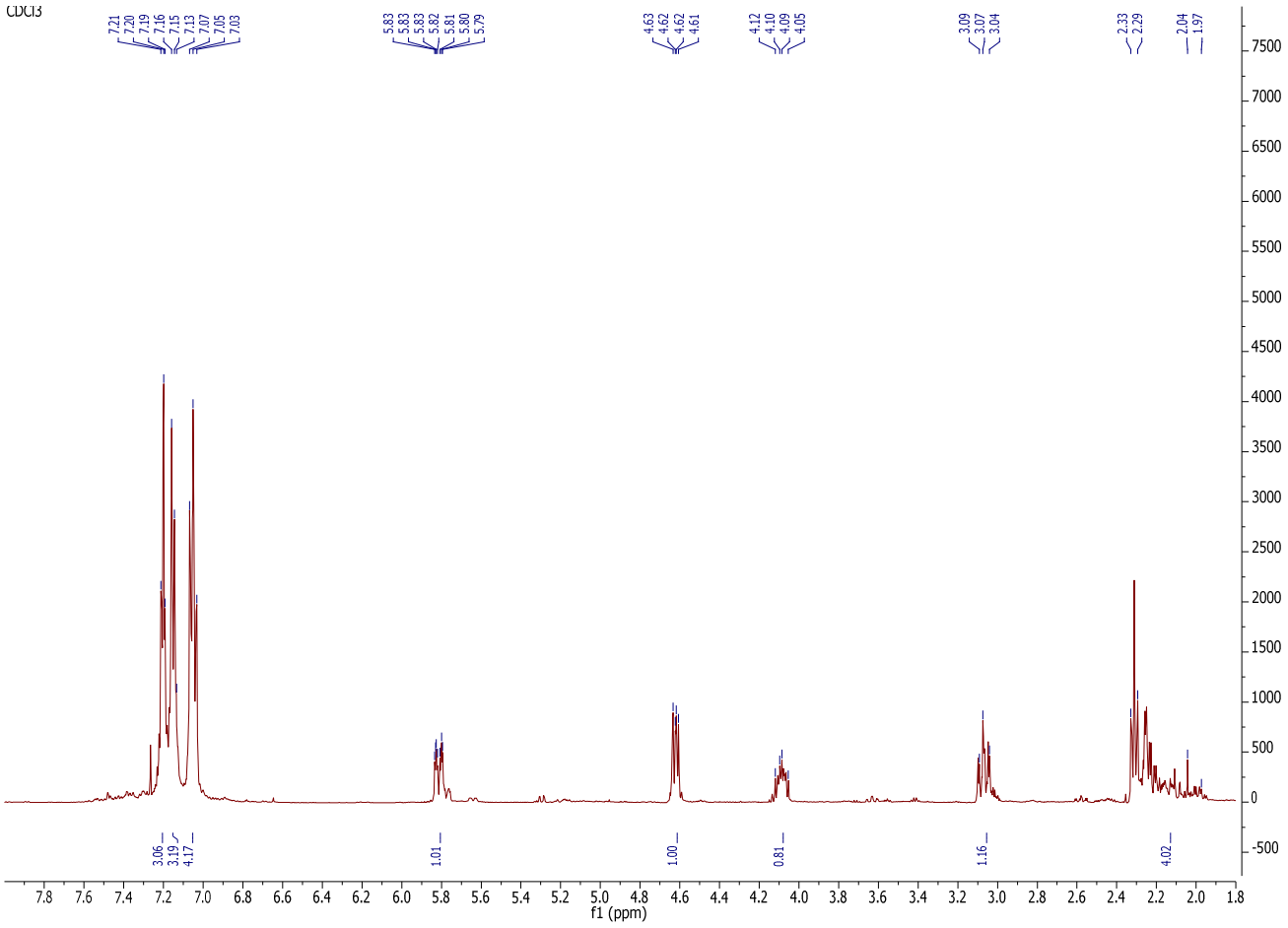

CDCl3
130.82
130.58
122.10
119.63
118.55
113.83
113.29
109.29
62.83
55.34
55.08
49.91
30.22
20.46
f1 (ppm)

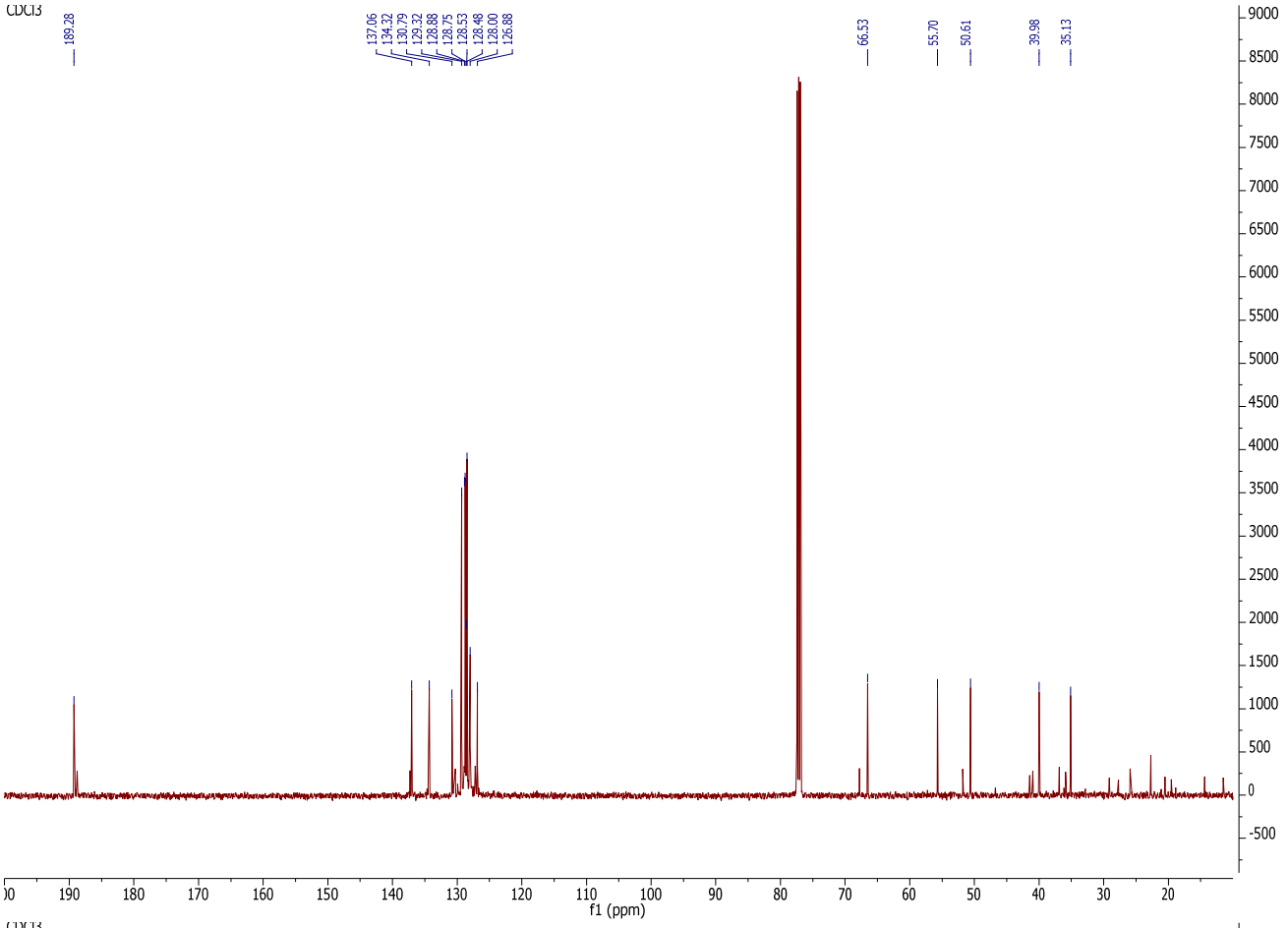

f2 (ppm)
f1 (ppm)

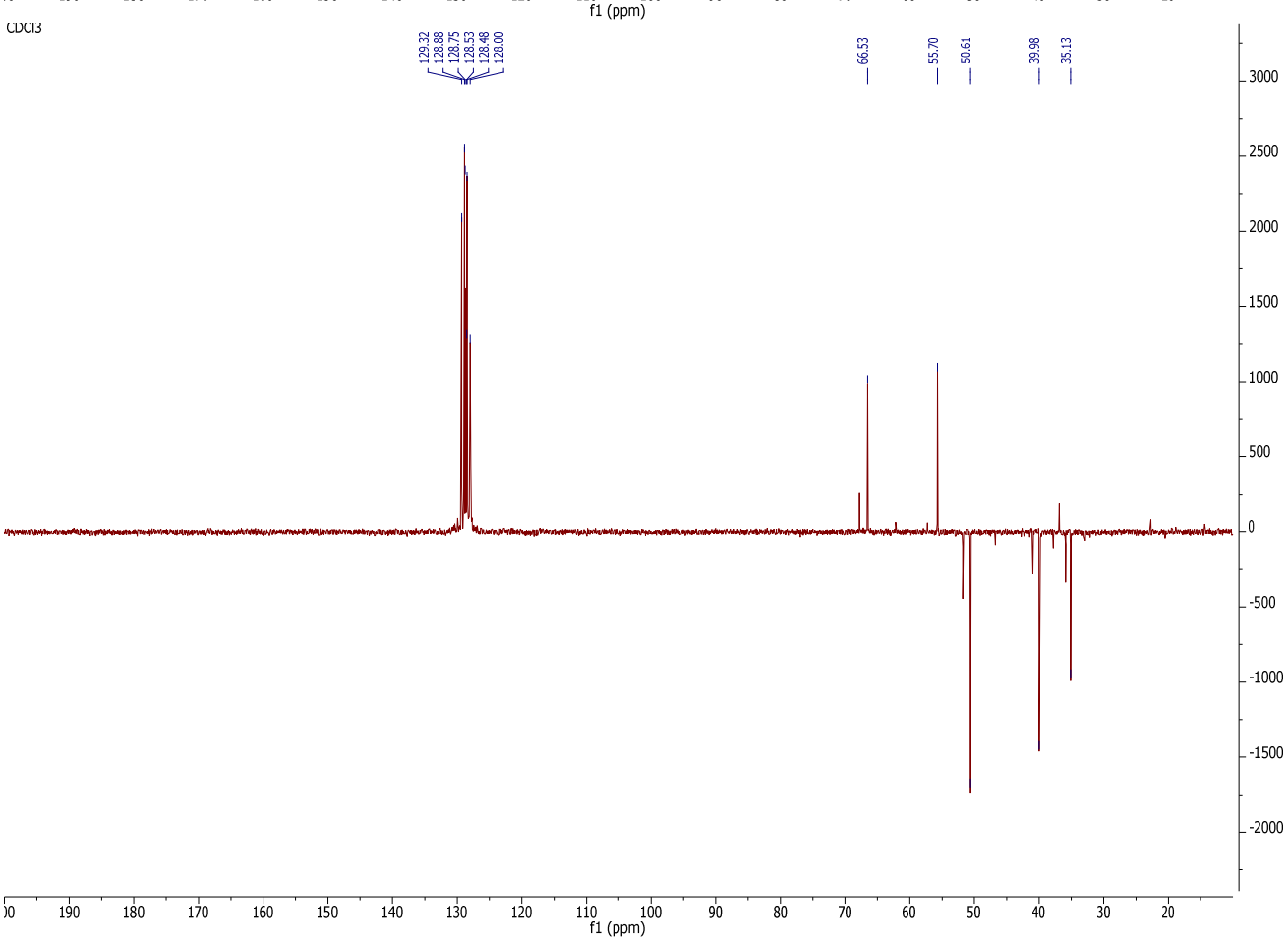

f2 (ppm)
f1 (ppm)

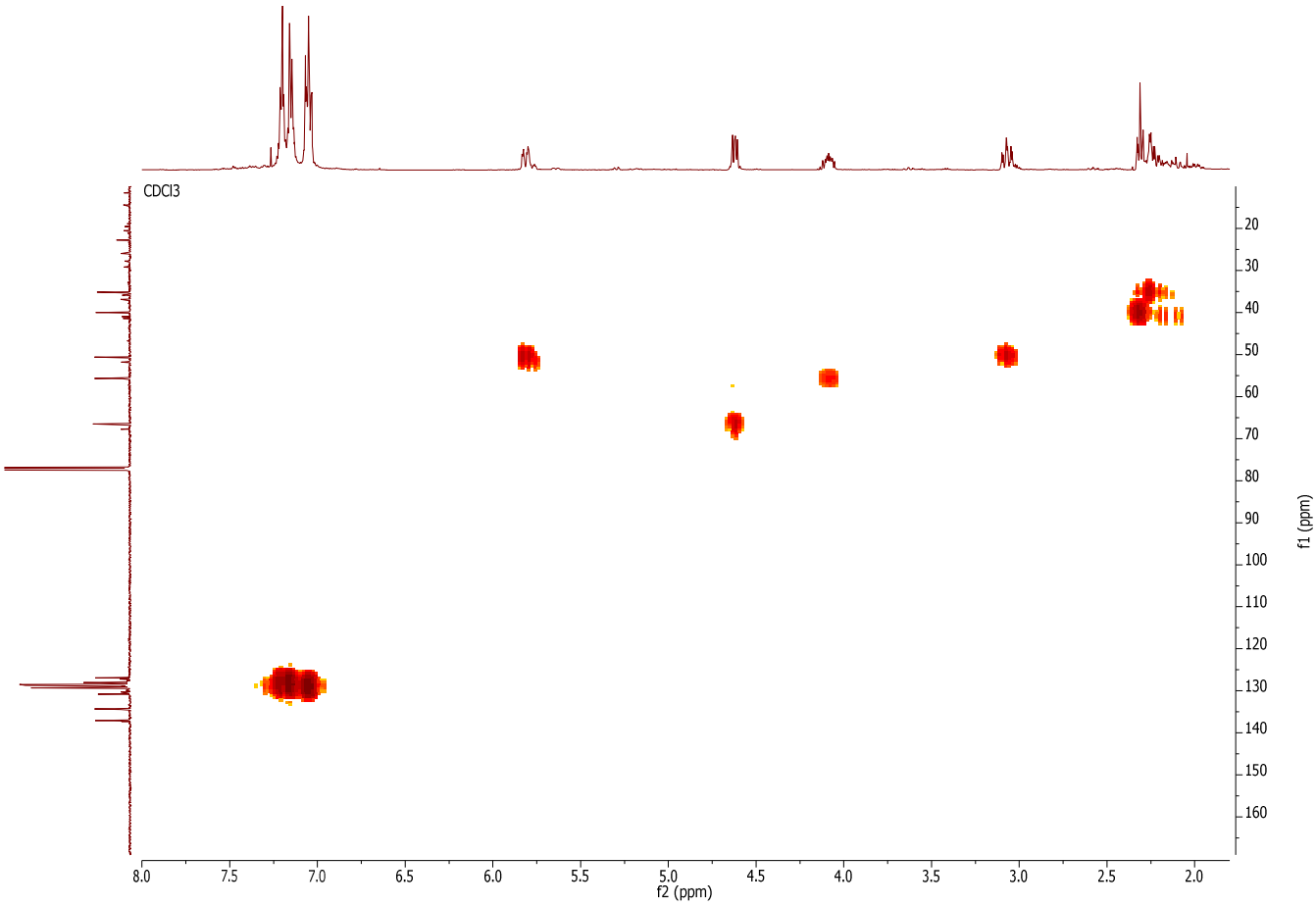

Cl
N
S
S

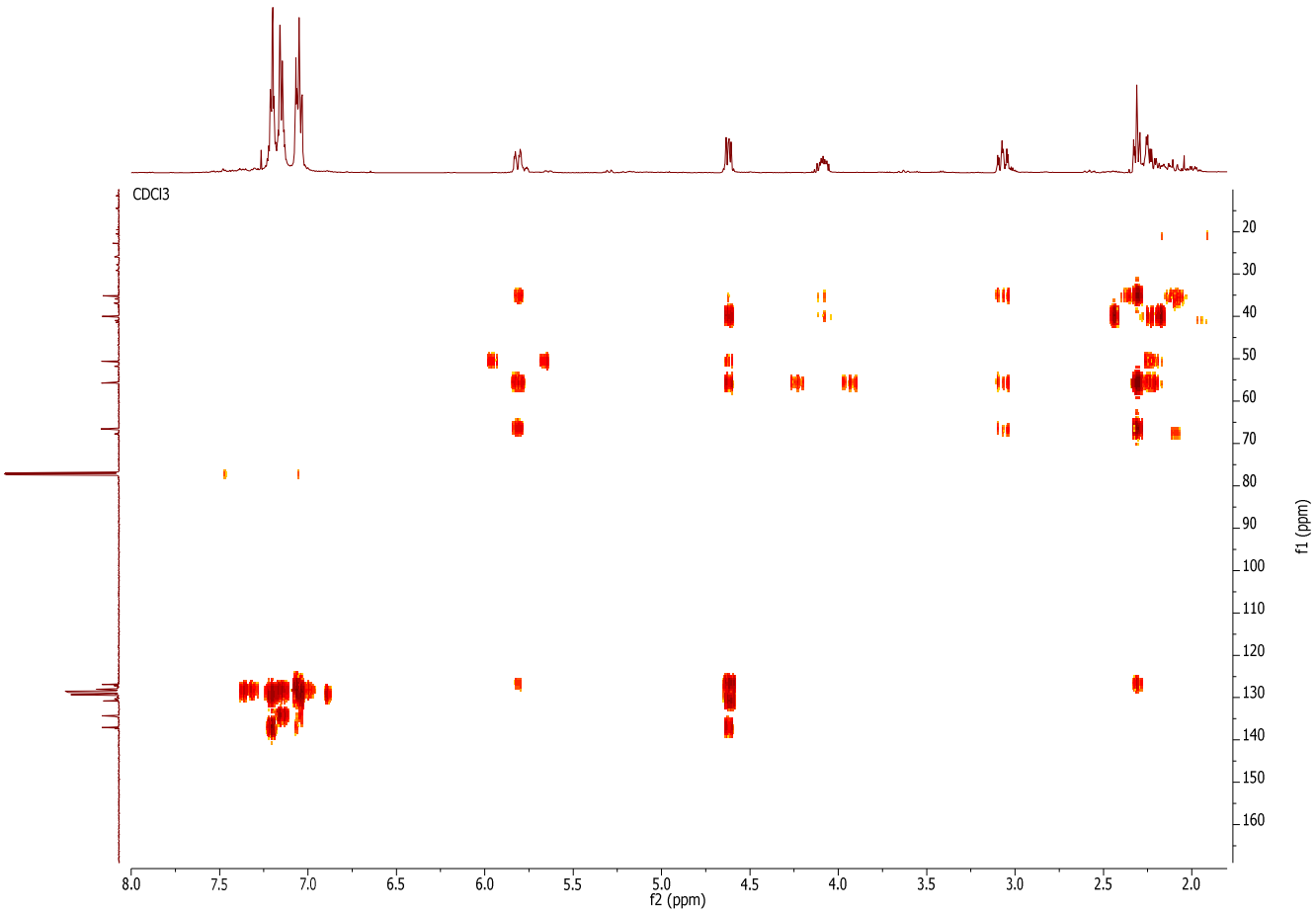
4a

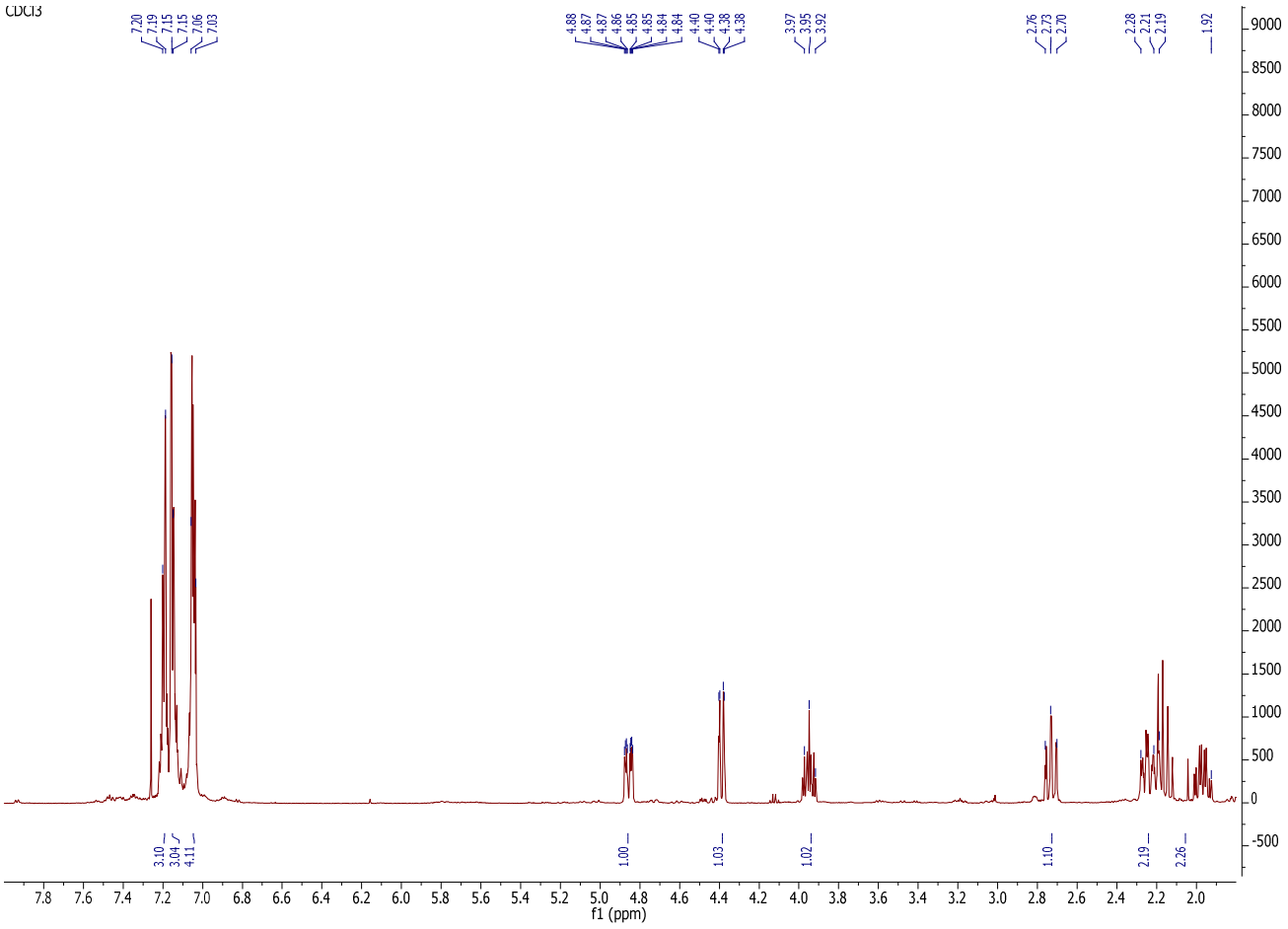

CDCl3
7.21
7.20
7.19
7.16
7.15
7.13
7.07
7.05
7.03
5.83
5.83
5.83
5.82
5.81
5.80
5.79
4.63
4.62
4.62
4.61
4.12
4.10
4.09
4.05
3.09
3.07
3.04
2.33
2.29
2.04
1.97
3.06
3.19
4.17
1.01
1.00
0.81
1.16
4.02
f1 (ppm)

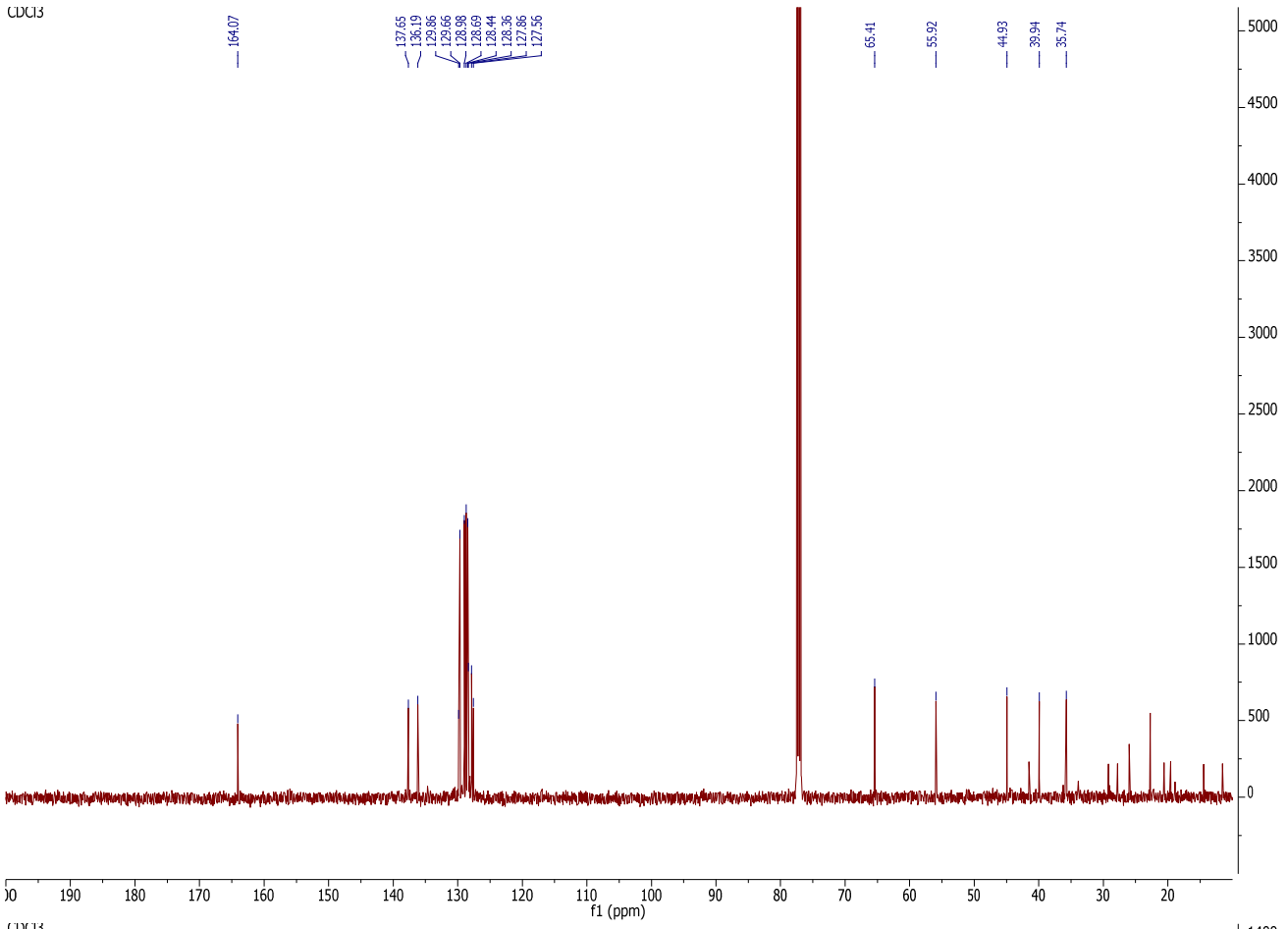

CDCl3
189.28
137.06
134.32
130.79
129.32
128.88
128.75
128.53
128.48
128.00
126.88
66.53
55.70
50.61
39.98
35.13
f1 (ppm)

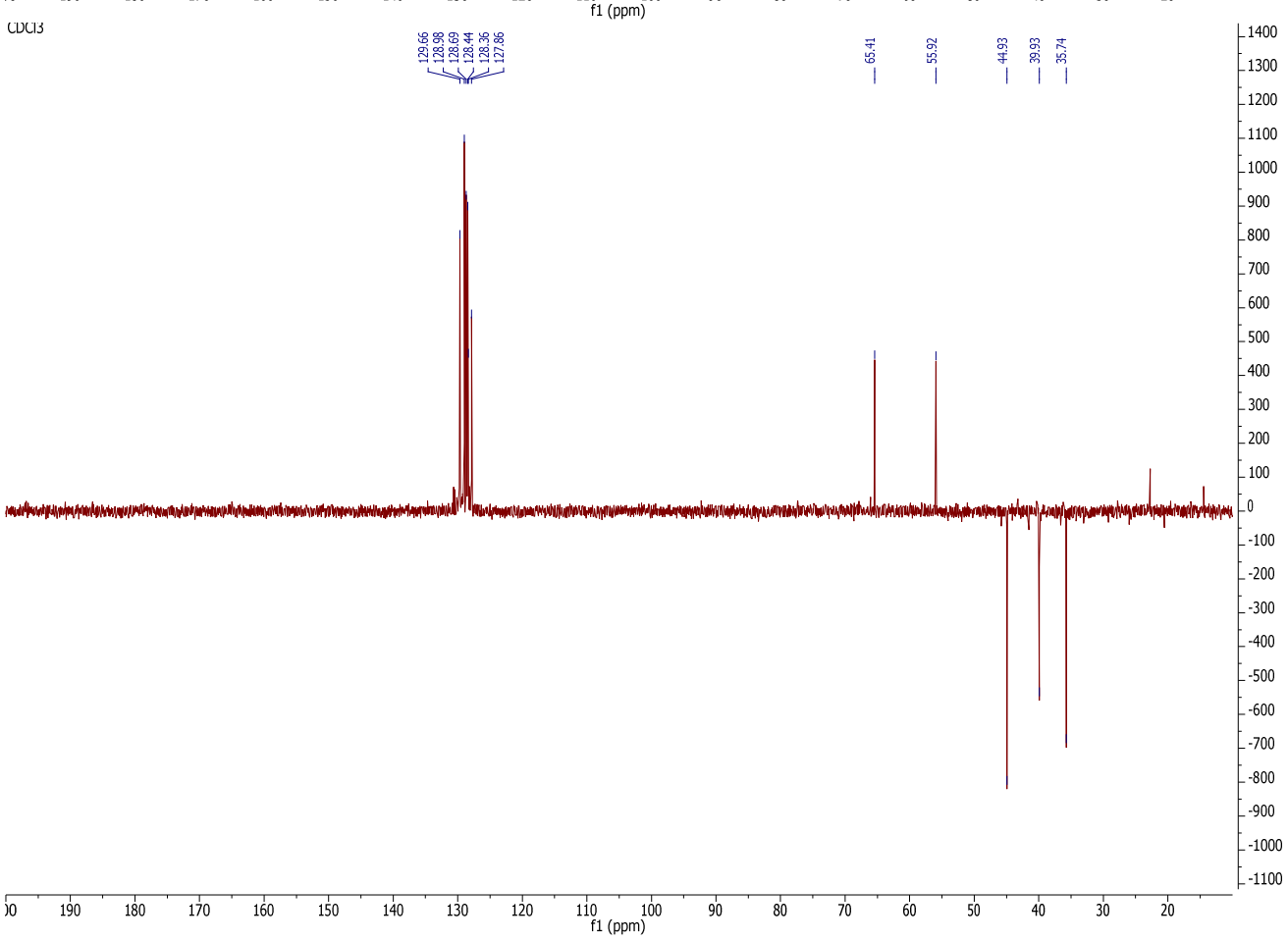

CDCl3
129.32
128.88
128.75
128.53
128.48
128.00
66.53
55.70
50.61
39.98
35.13
f1 (ppm)

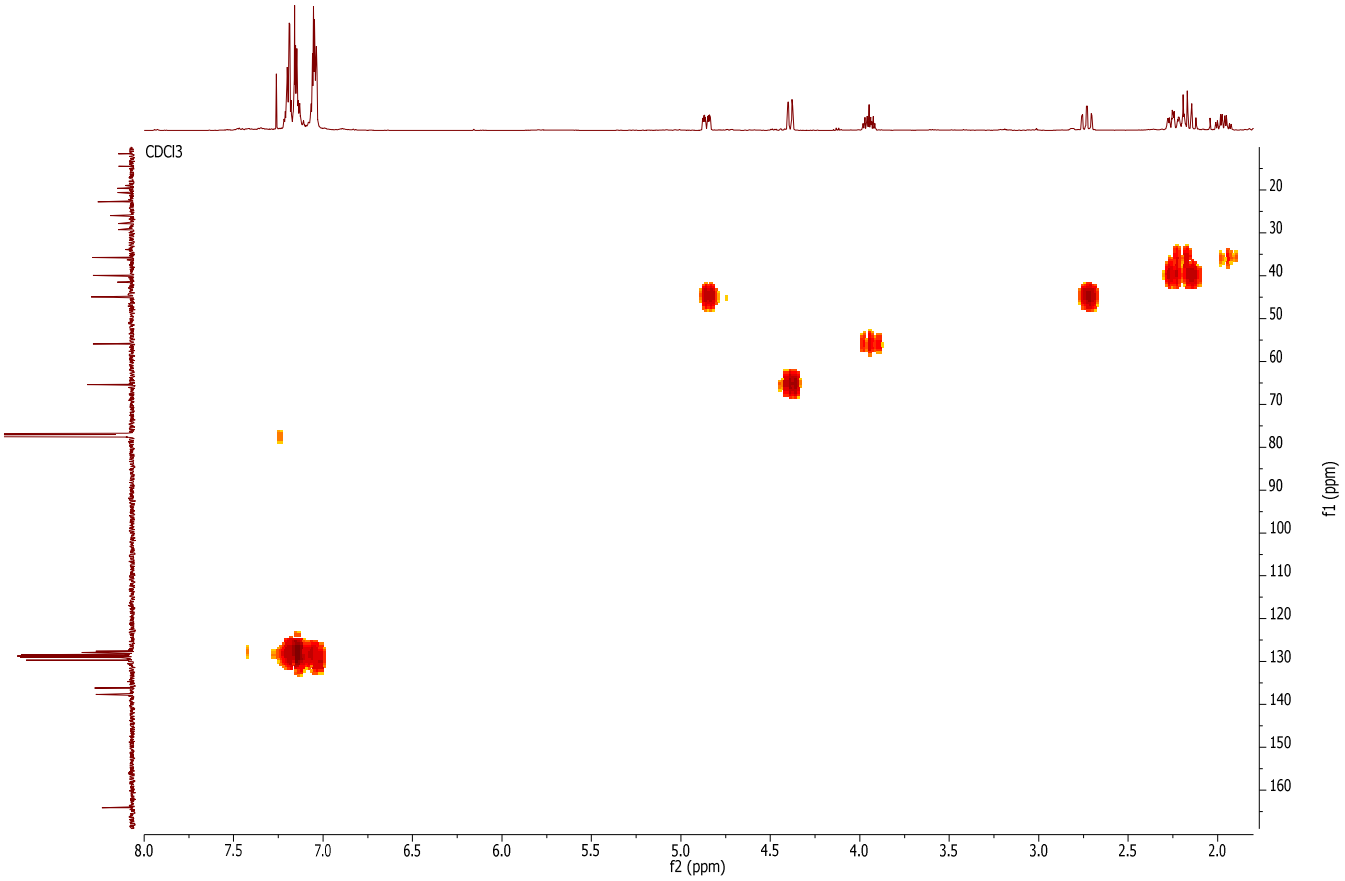

CDCl3
f2 (ppm)
f1 (ppm)

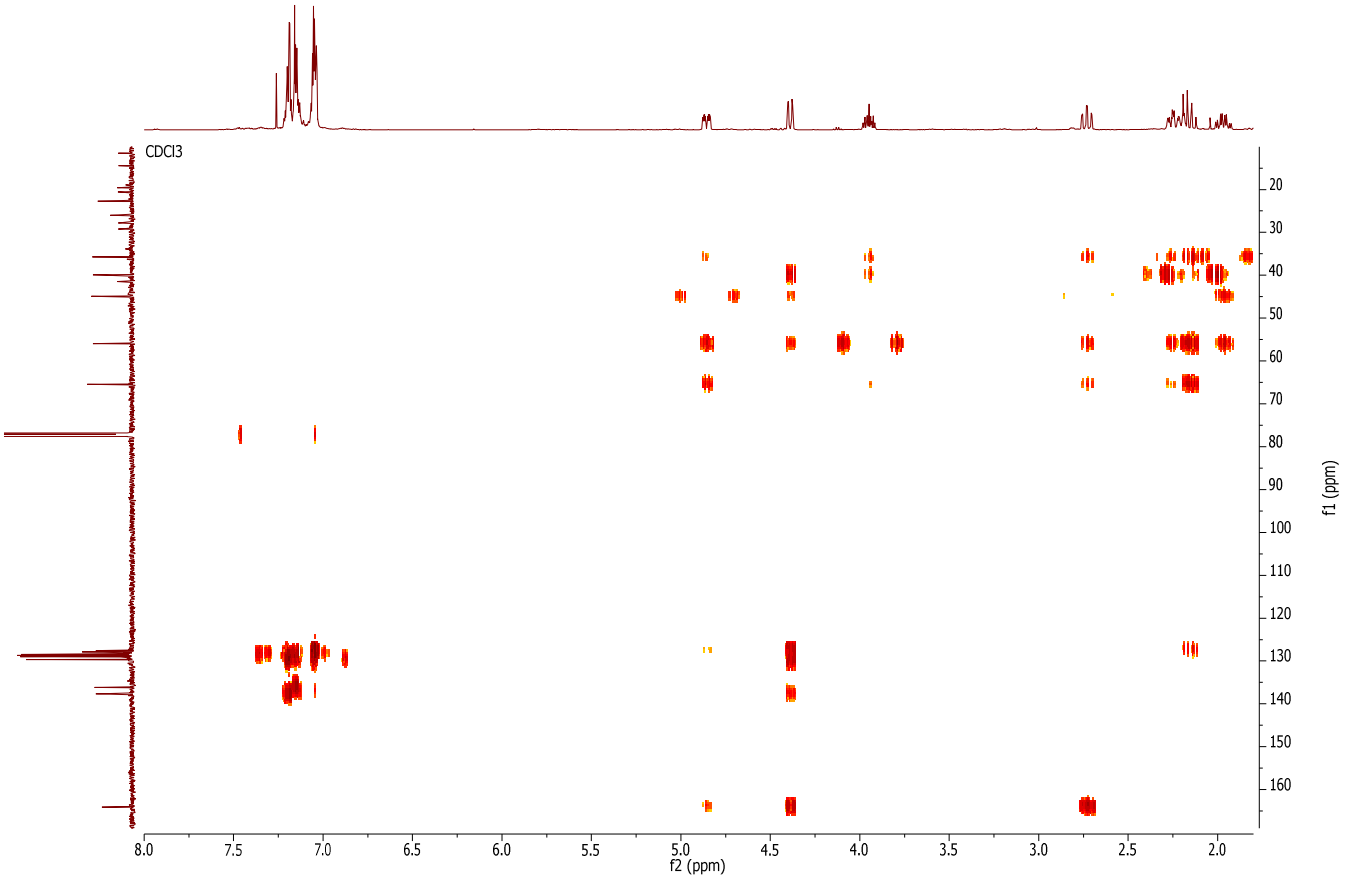

CDCl3
f2 (ppm)
f1 (ppm)

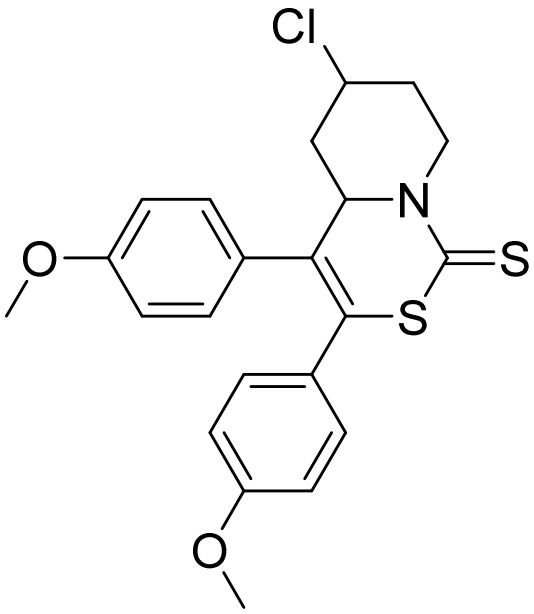

CDCl3
7.20
7.19
7.15
7.15
7.06
7.03
4.88
4.87
4.87
4.86
4.85
4.85
4.84
4.84
4.40
4.40
4.38
4.38
3.97
3.95
3.92
2.76
2.73
2.70
2.28
2.21
2.19
1.92
3.10
3.04
4.11
1.00
1.03
1.02
1.10
2.19
2.26
f1 (ppm)


CDCl3
164.07
137.65
136.19
129.86
129.66
128.98
128.69
128.44
128.36
127.86
127.56
65.41
55.92
44.93
39.94
35.74
f1 (ppm)

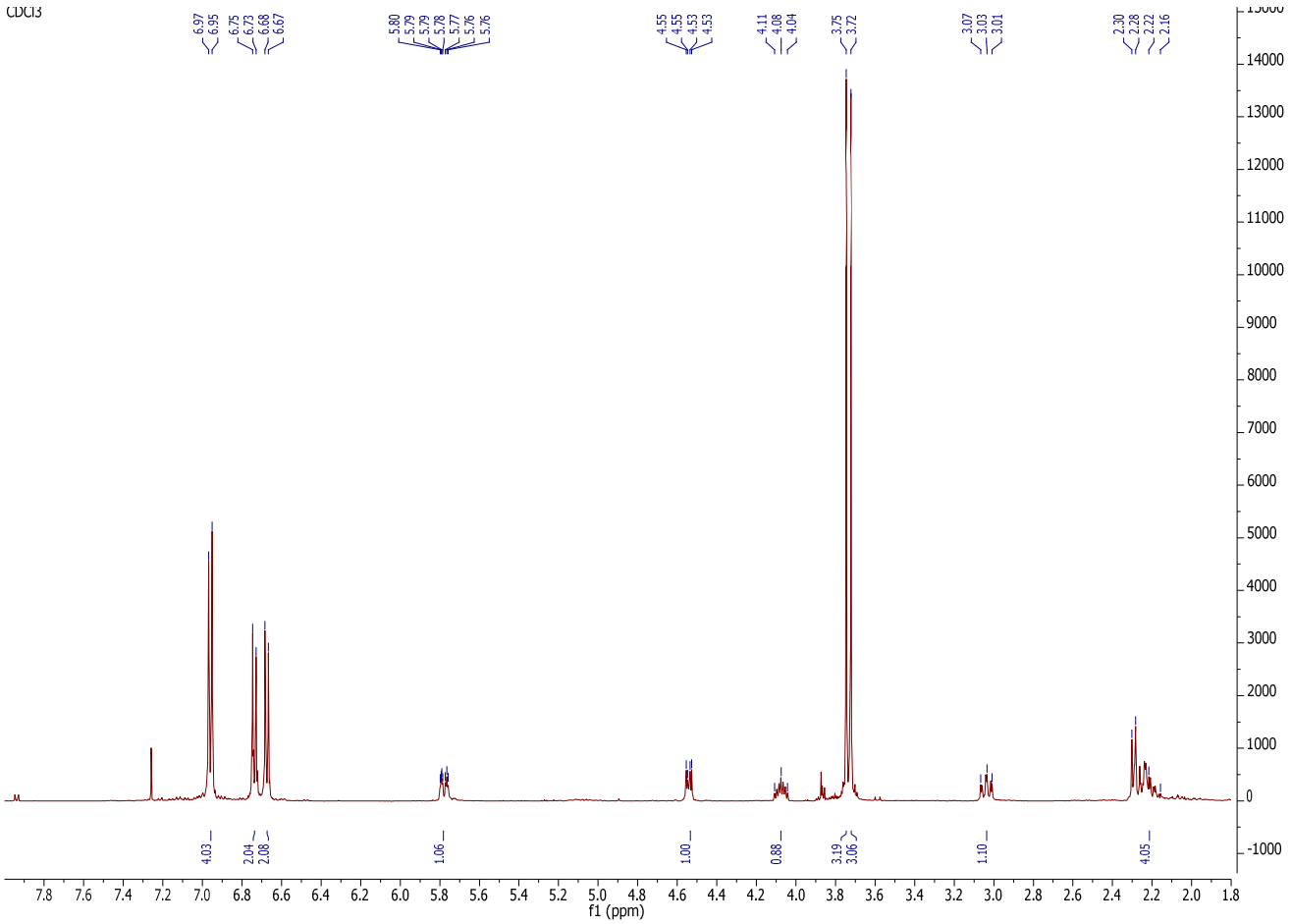

CDCl3
129.66
128.98
128.69
128.44
128.36
127.86
65.41
55.92
44.93
39.93
35.74
f1 (ppm)

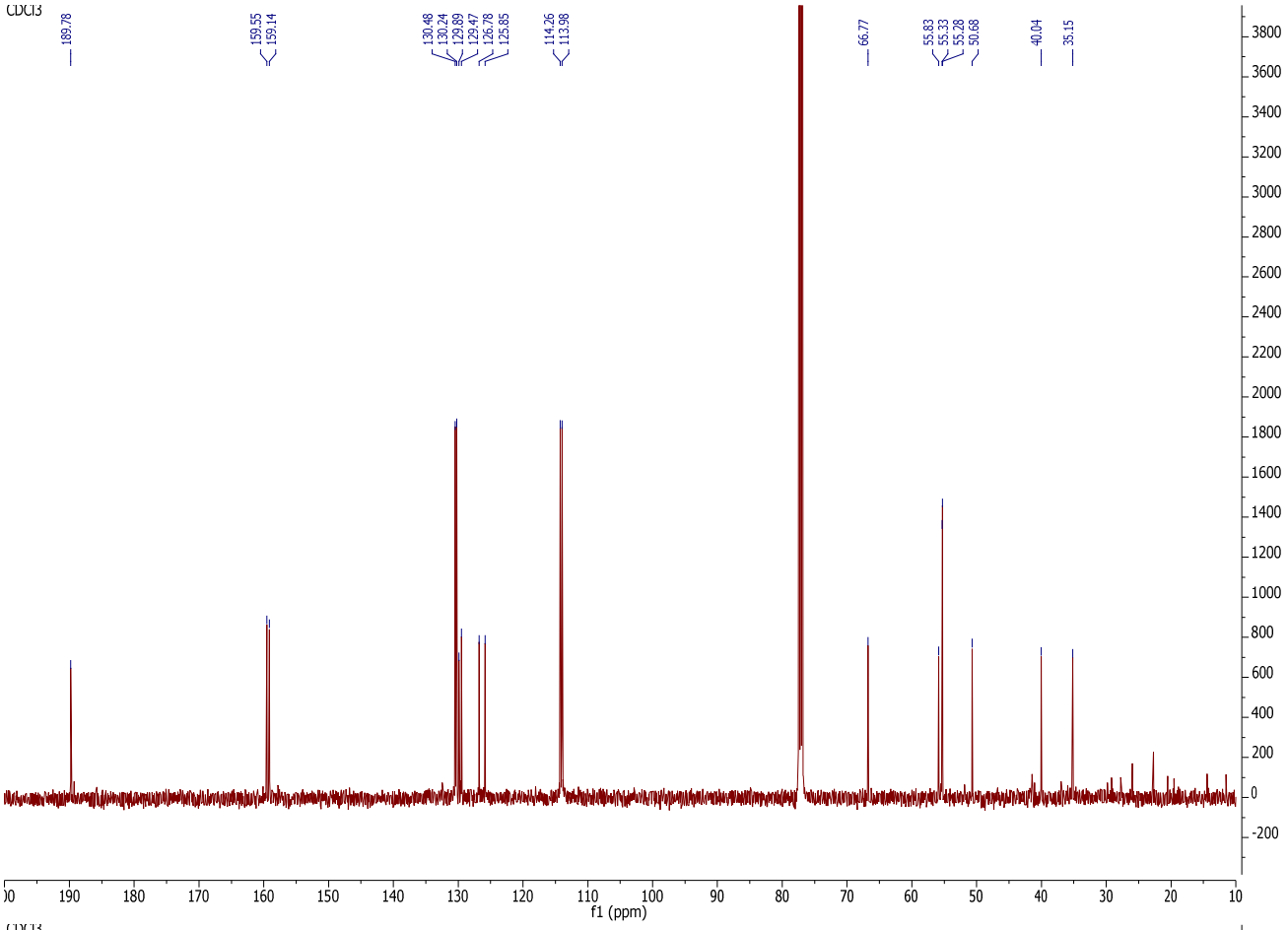

CDCl3
f2 (ppm)
f1 (ppm)

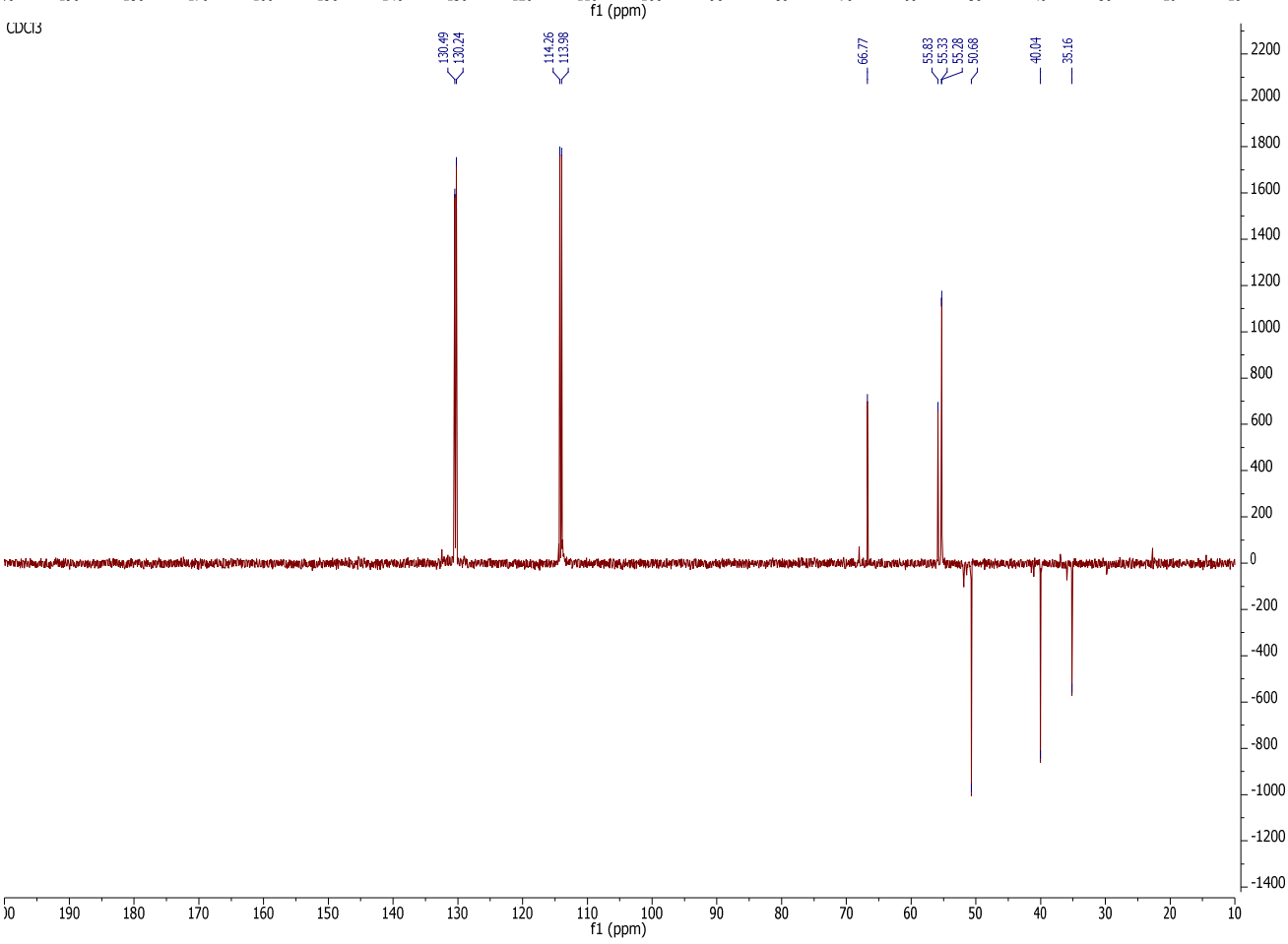

CDCl3
f2 (ppm)
f1 (ppm)

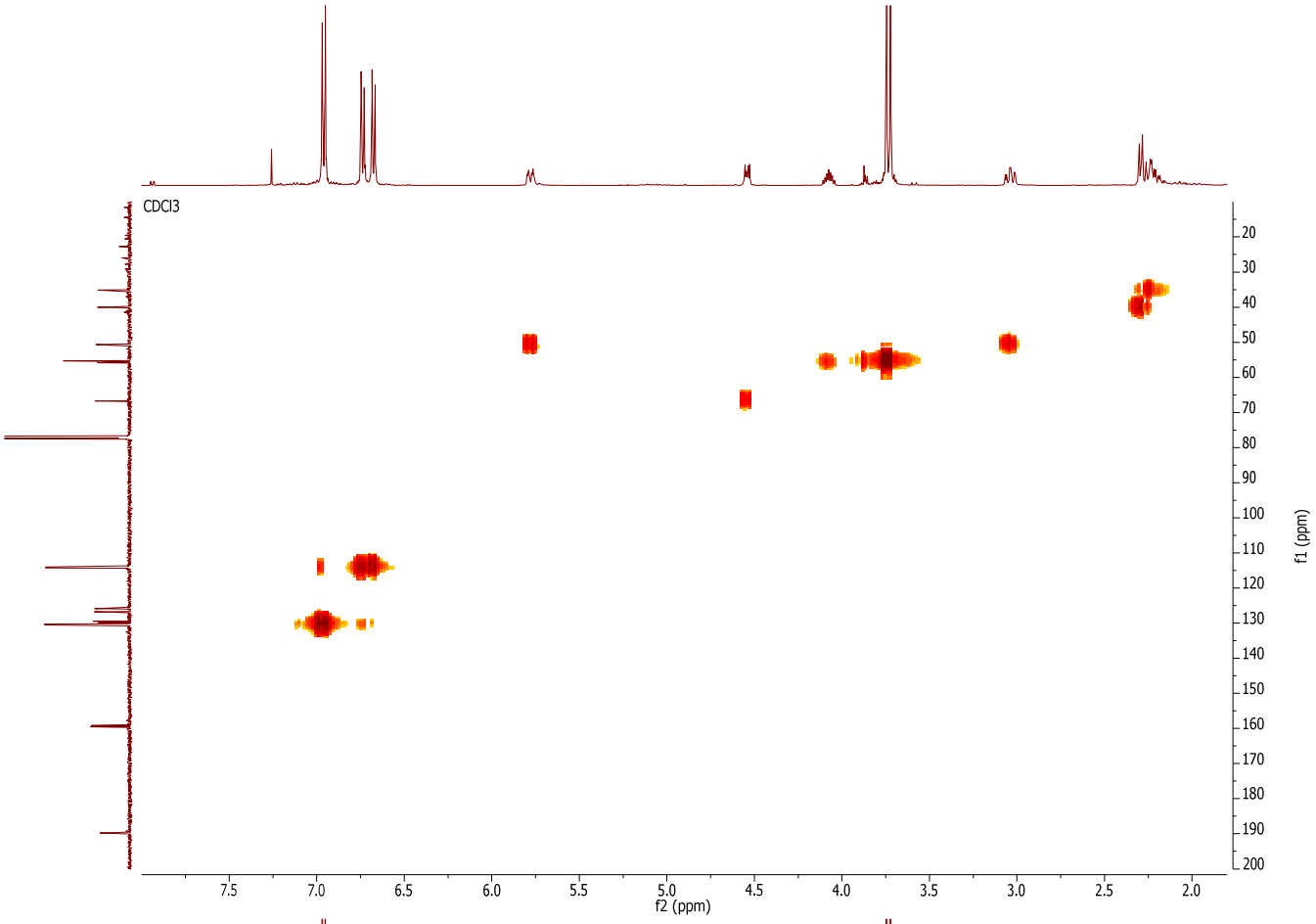

Cl
N
O
S
S
O

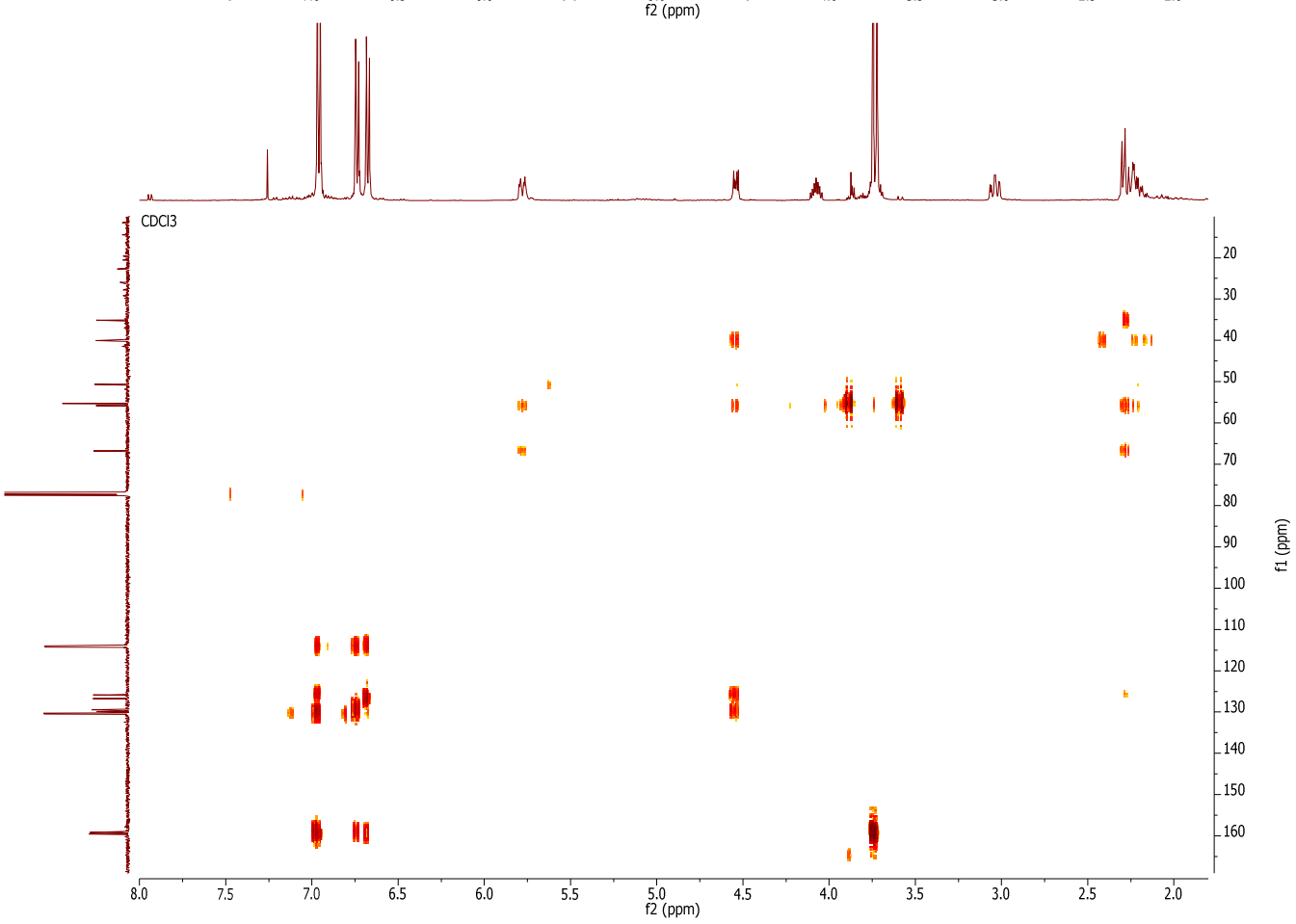
4b

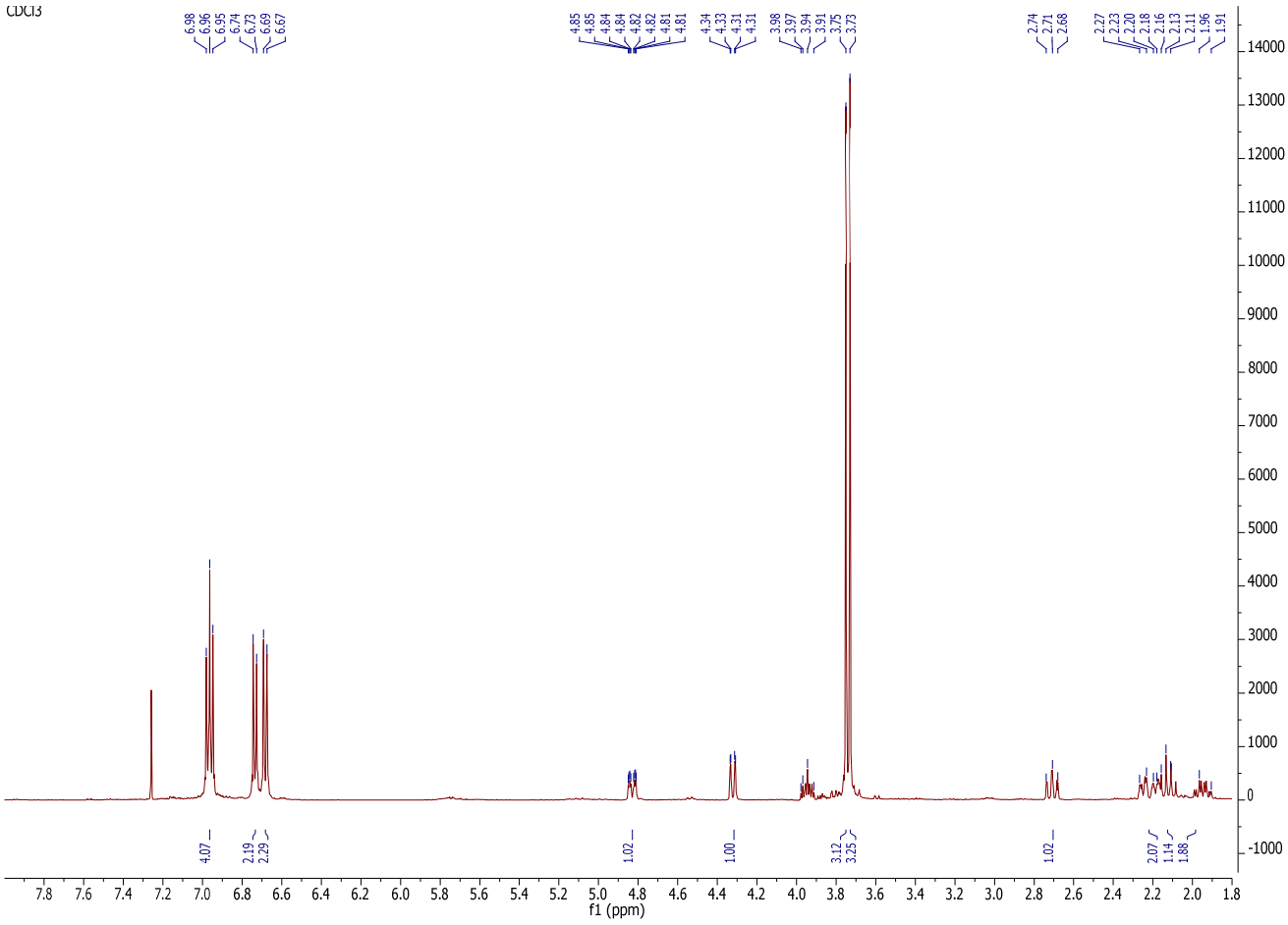

CDCl3
6.97
6.95
6.75
6.73
6.68
6.67
5.80
5.79
5.79
5.78
5.77
5.76
5.76
4.55
4.55
4.53
4.53
4.11
4.08
4.04
3.75
3.72
3.07
3.03
3.01
2.30
2.28
2.22
2.16
4.03
2.04
2.08
1.06
1.00
0.88
3.19
3.06
1.10
4.05
f1 (ppm)

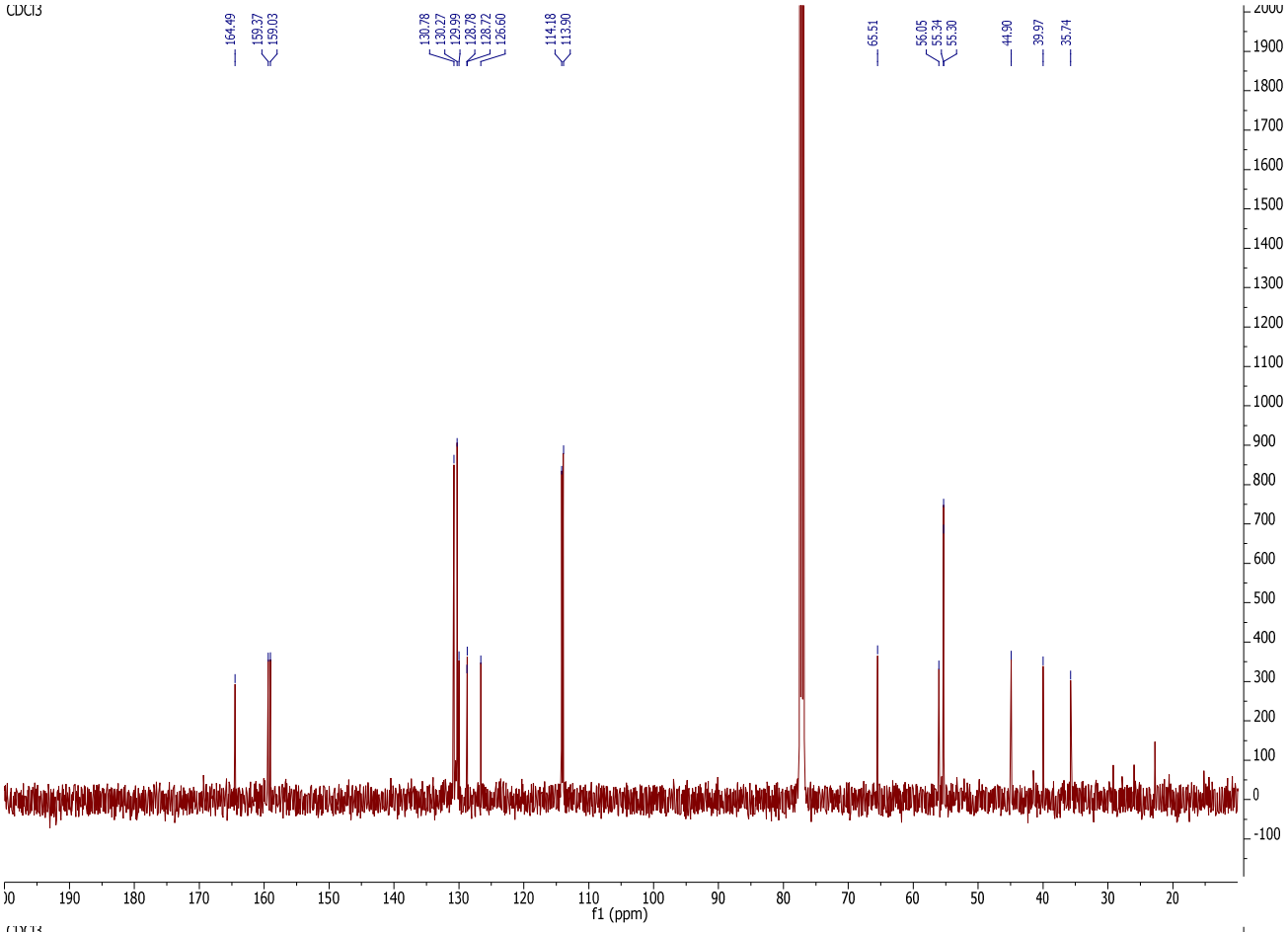

CDCl3
189.78
159.55
159.14
130.48
130.24
129.89
129.47
126.78
125.85
114.26
113.98
66.77
55.83
55.33
55.28
50.68
40.04
35.15
f1 (ppm)

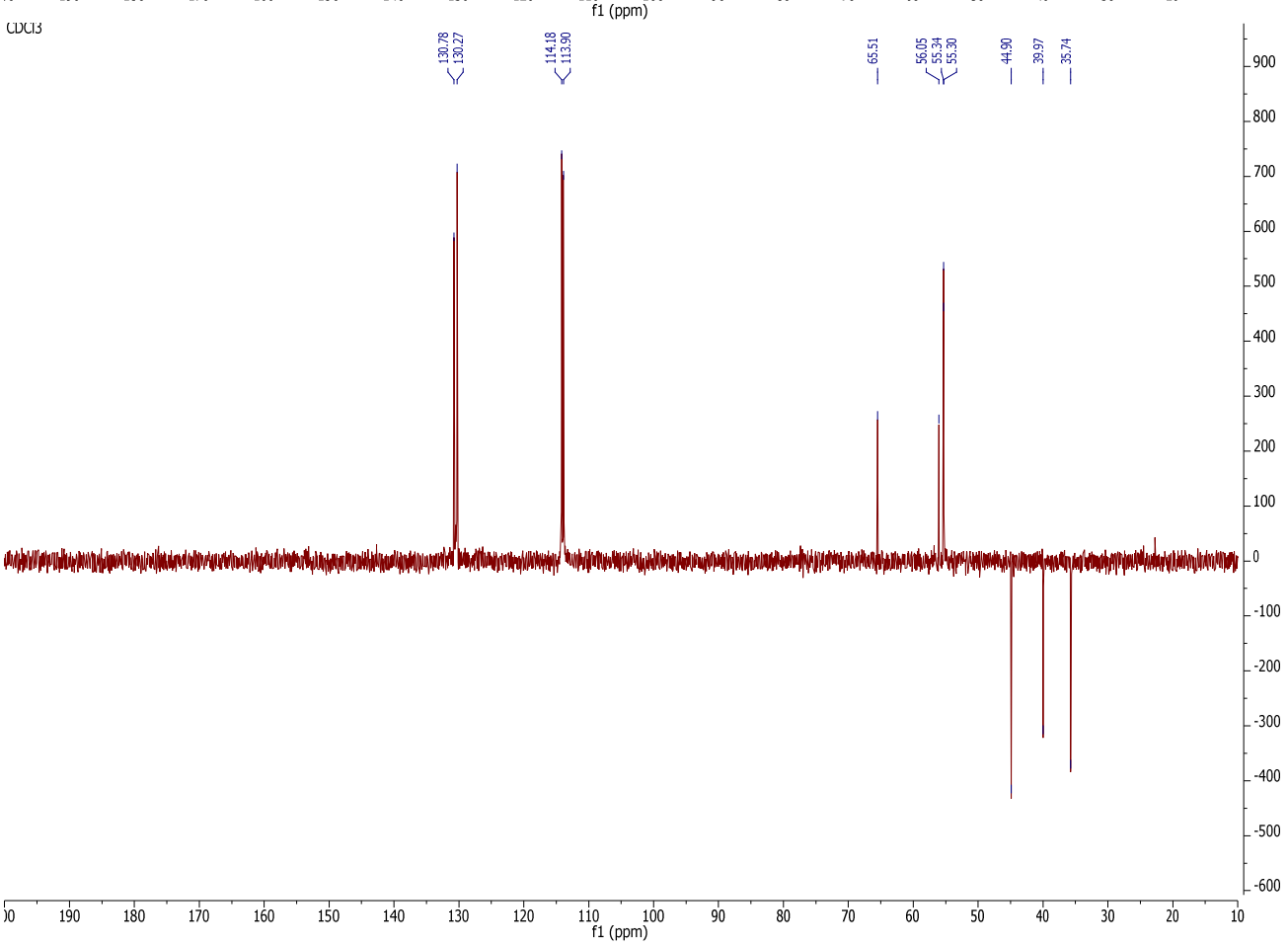

CDCl3
130.49
130.24
114.26
113.98
66.77
55.83
55.33
55.28
50.68
40.04
35.16
f1 (ppm)

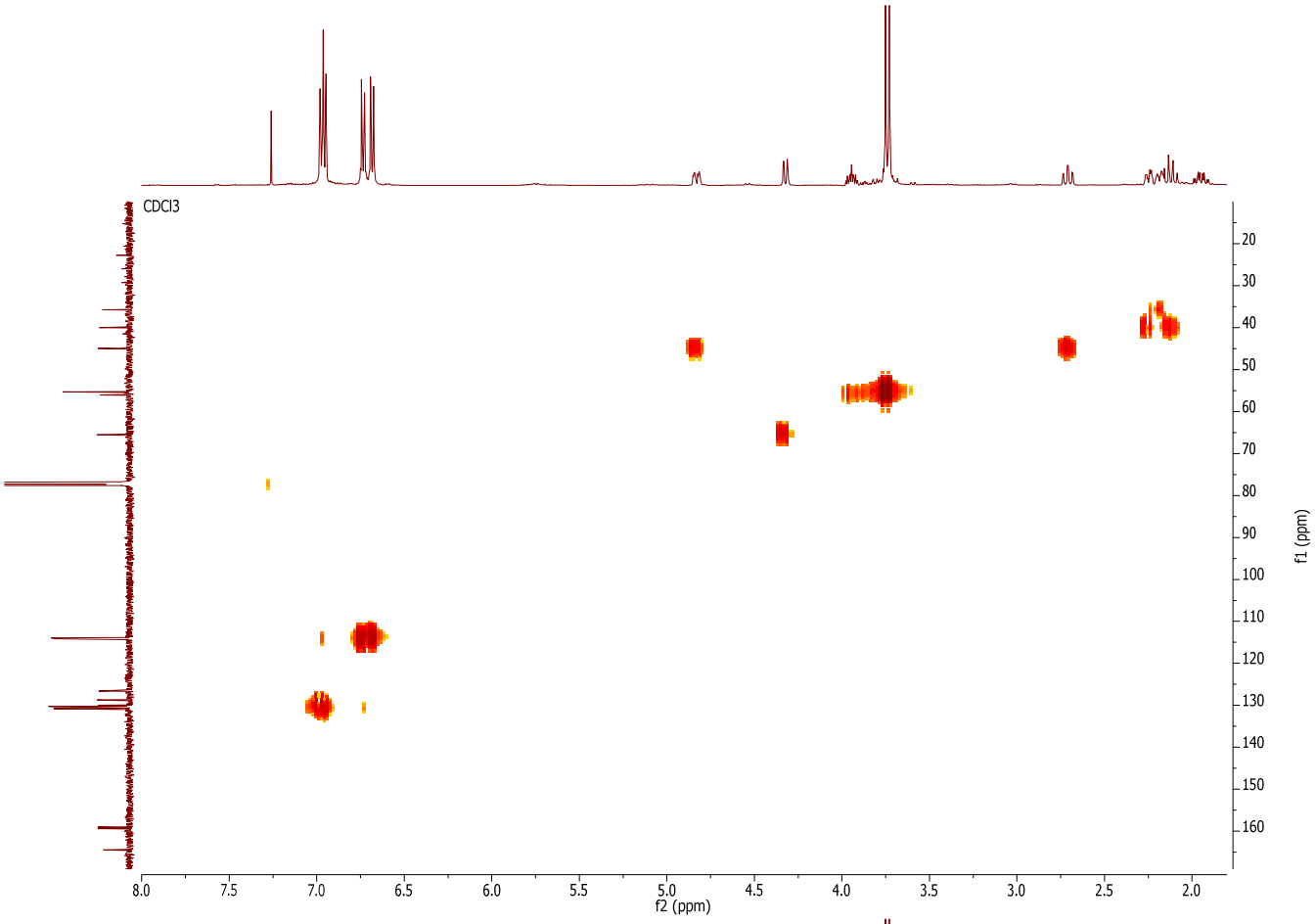

CDCl3
f2 (ppm)
f1 (ppm)

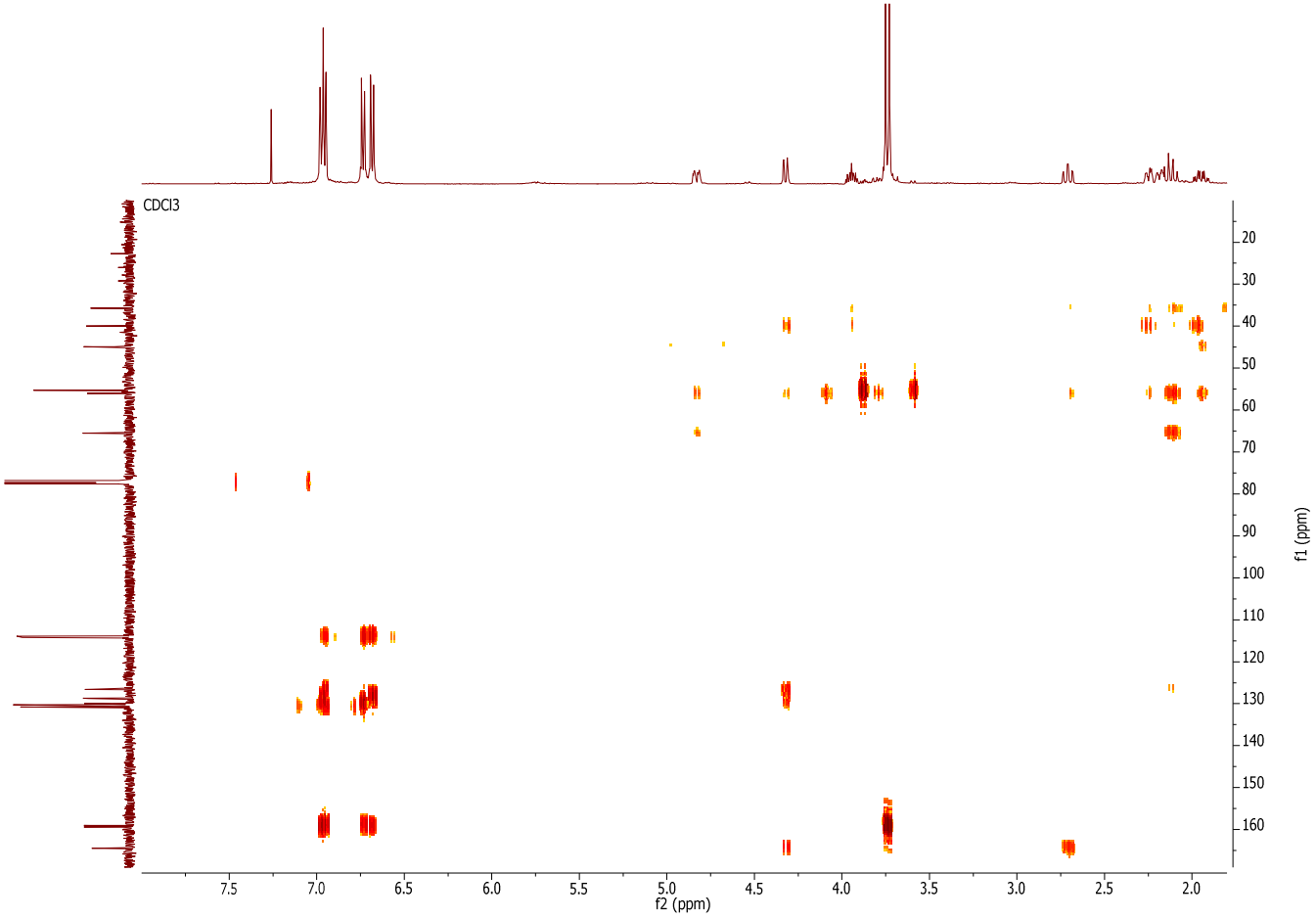

CDCl3
f2 (ppm)
f1 (ppm)

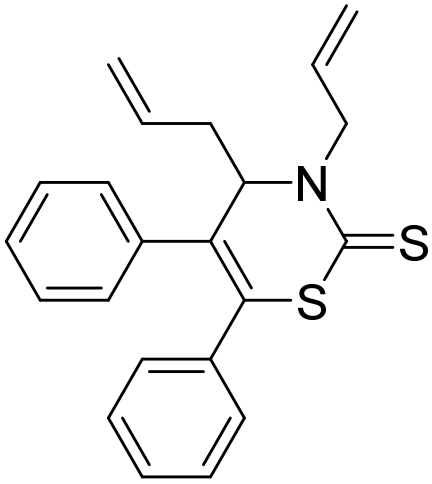

CDCl3
6.98
6.96
6.95
6.74
6.73
6.69
6.67
4.85
4.85
4.84
4.84
4.82
4.82
4.81
4.81
4.34
4.33
4.31
4.31
3.98
3.97
3.94
3.91
3.75
3.73
2.74
2.71
2.68
2.27
2.23
2.20
2.18
2.16
2.13
2.11
1.96
1.91
4.07
2.19
2.29
1.02
1.00
3.12
3.25
1.02
2.07
1.14
1.88
f1 (ppm)


CDCl3
164.49
159.37
159.03
130.78
130.27
129.99
128.78
128.72
126.60
114.18
113.90
65.51
56.05
55.34
55.30
44.90
39.97
35.74
f1 (ppm)

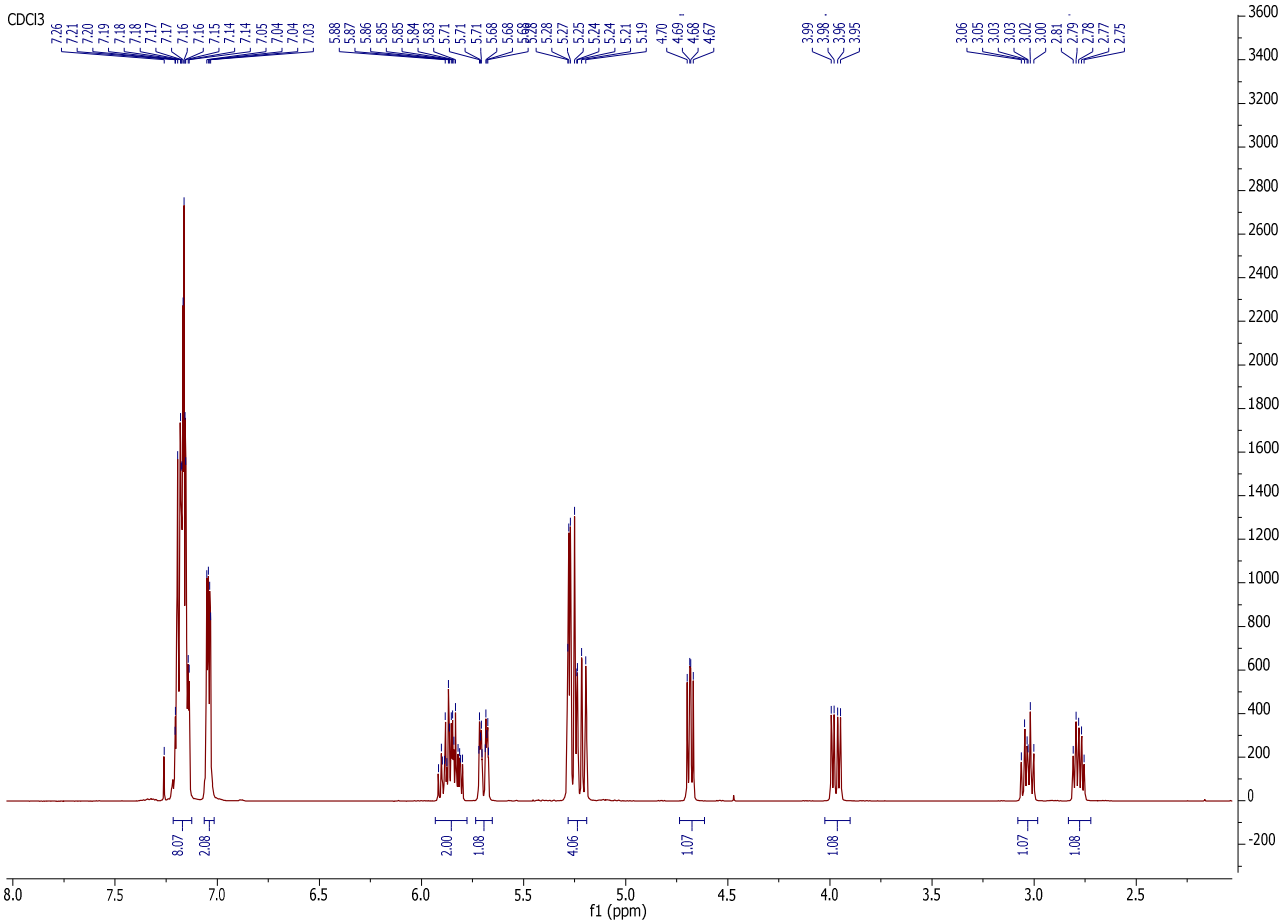

CDCl3
130.78
130.27
114.18
113.90
65.51
56.05
55.34
55.30
44.90
39.97
35.74
f1 (ppm)

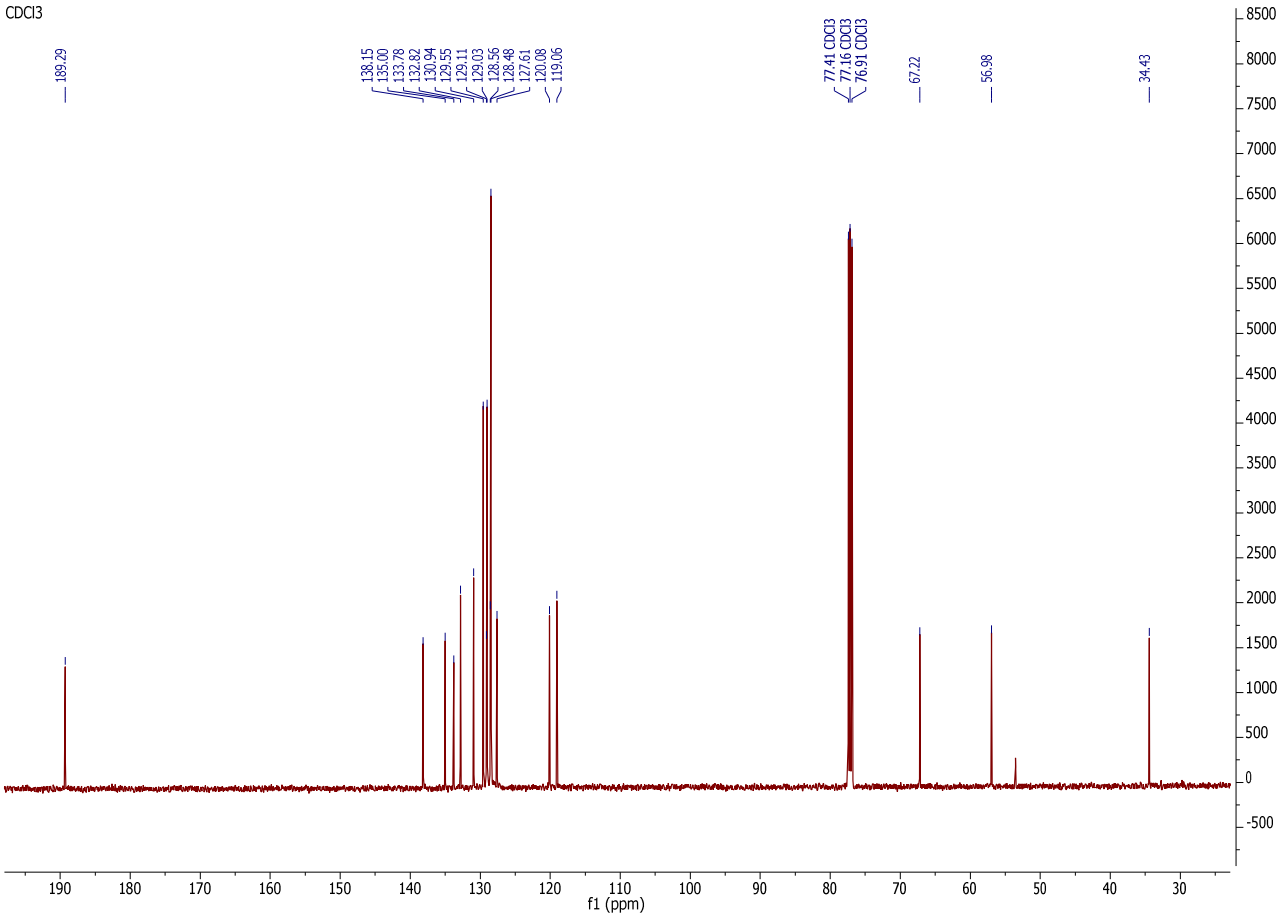

CDCl3
f2 (ppm)
f1 (ppm)

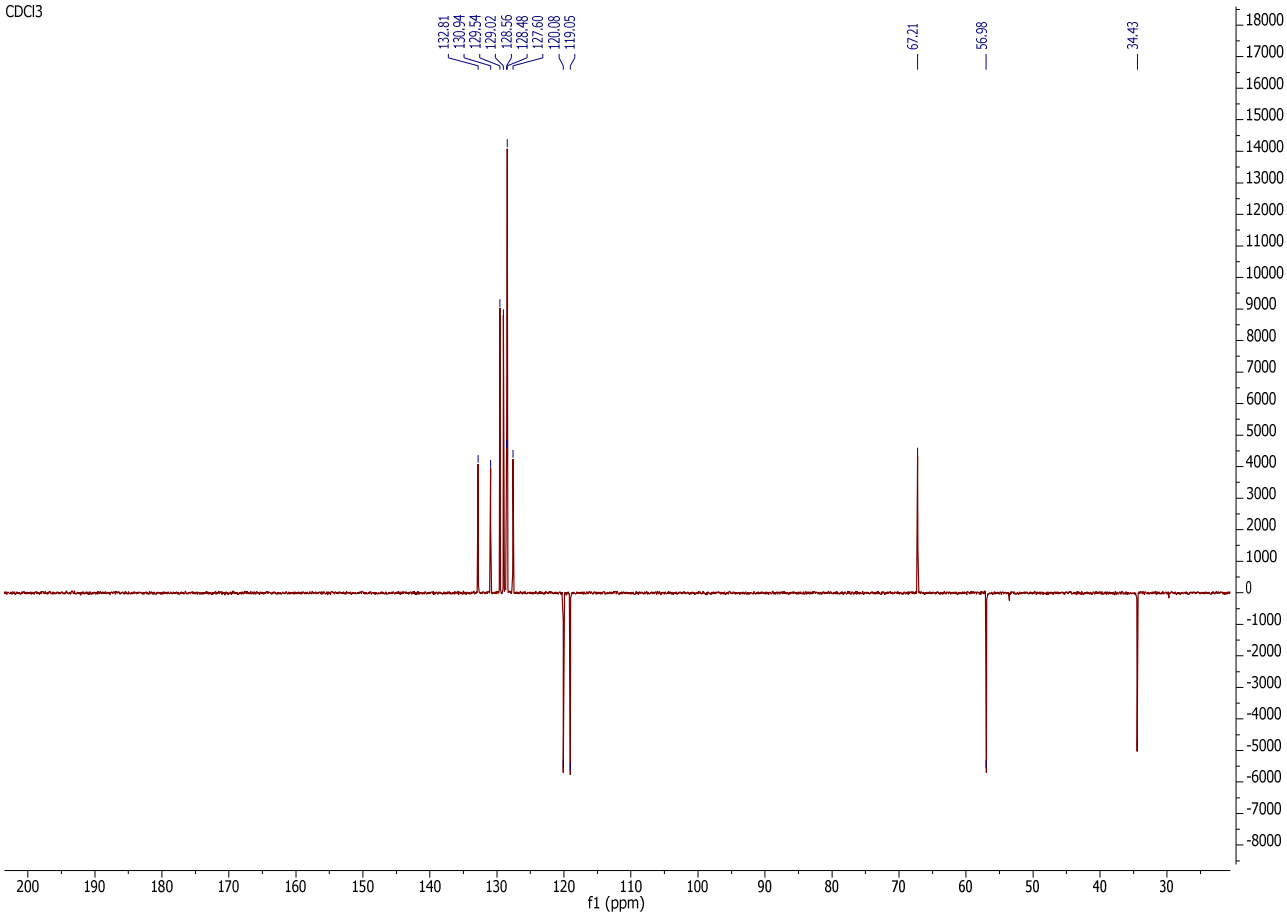

CDCl3
f2 (ppm)
f1 (ppm)

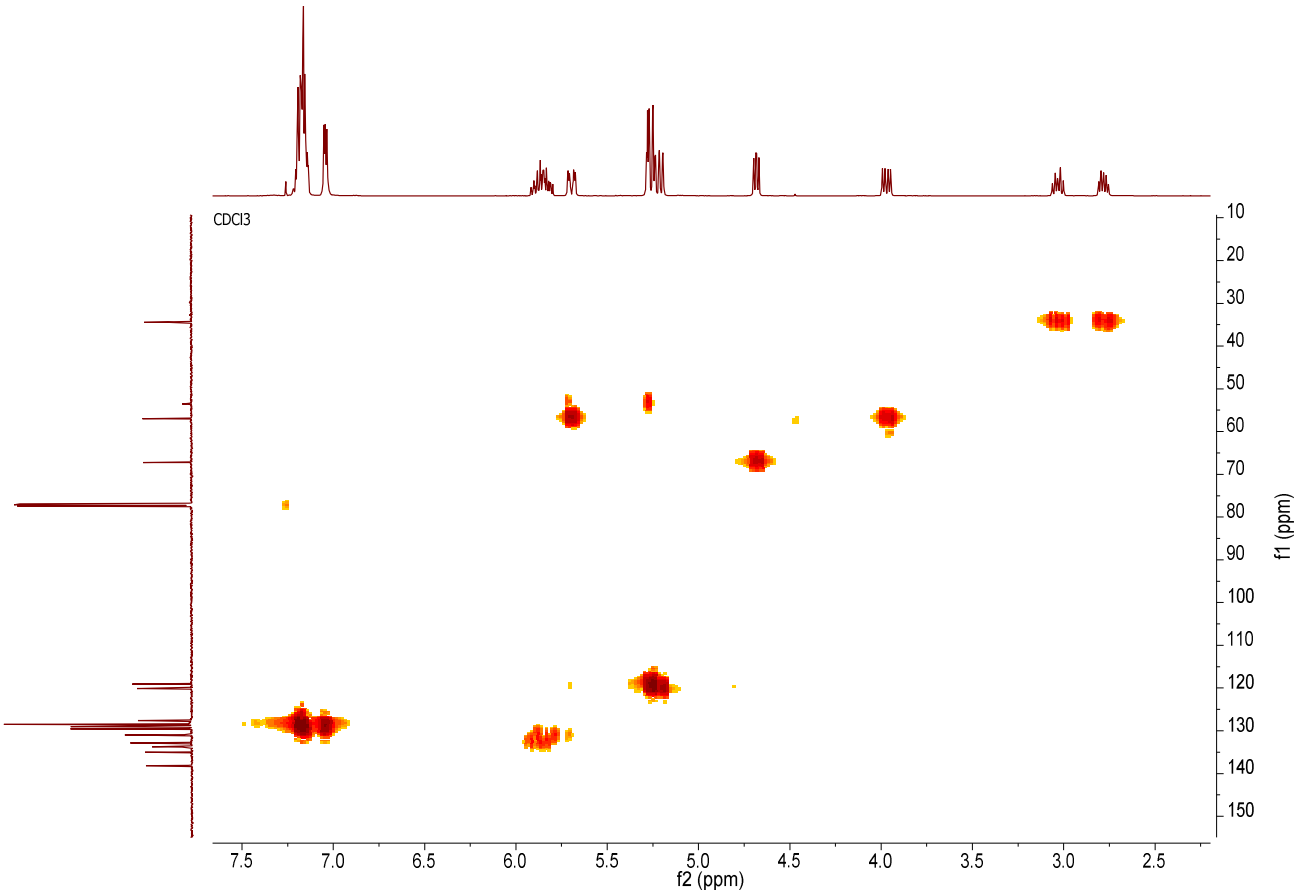


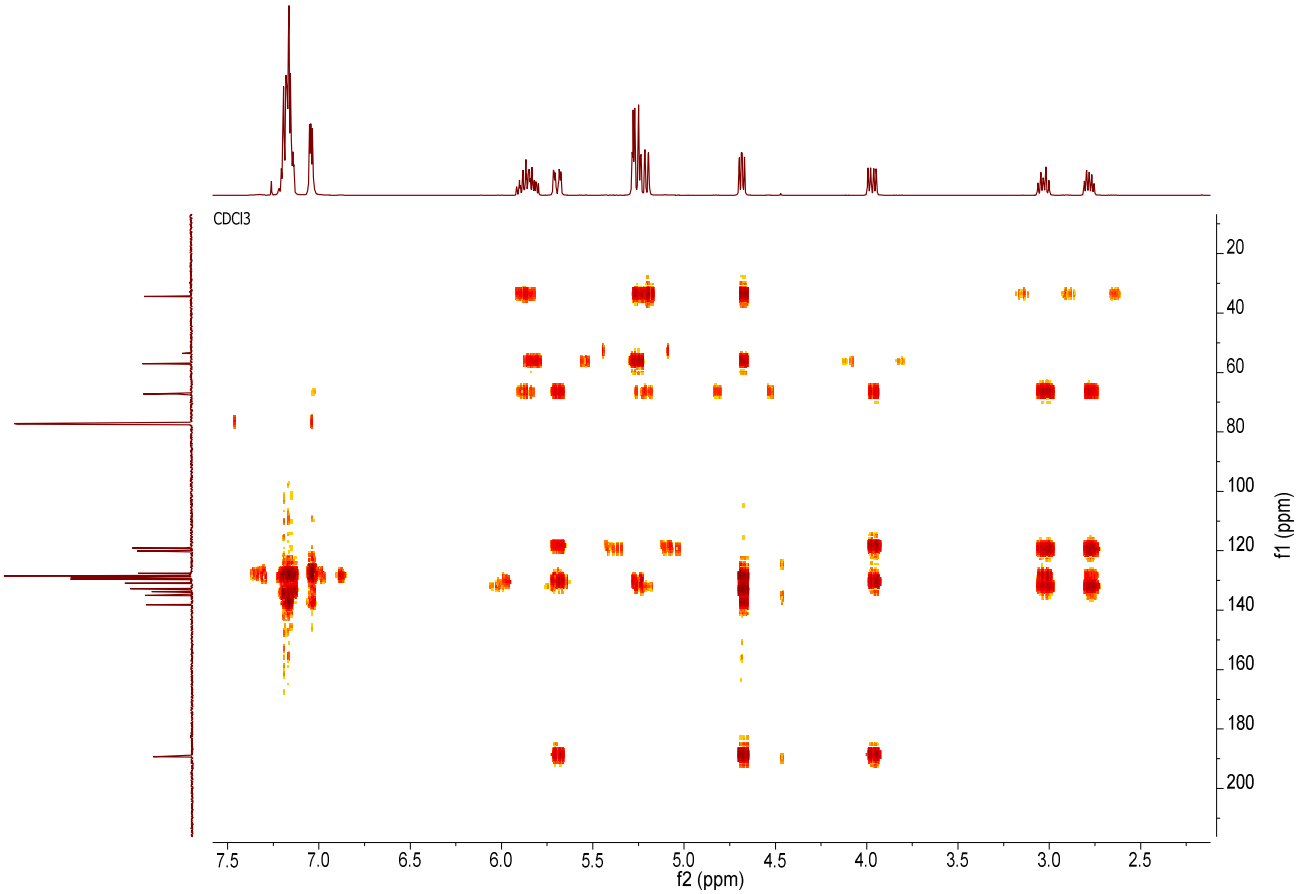
5a

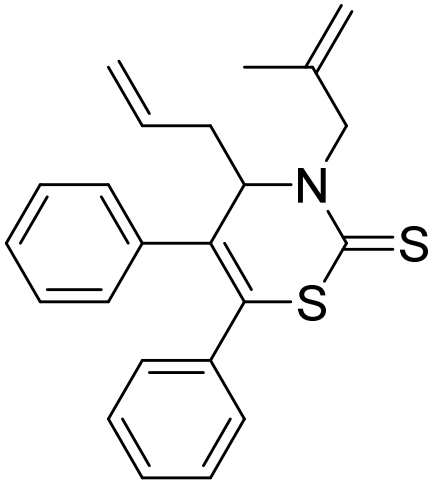



CDCl3
189.29
138.15
135.00
133.78
132.82
130.94
129.55
129.11
129.03
128.56
128.48
127.61
120.08
119.06
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
67.22
56.98
34.43
f1 (ppm)

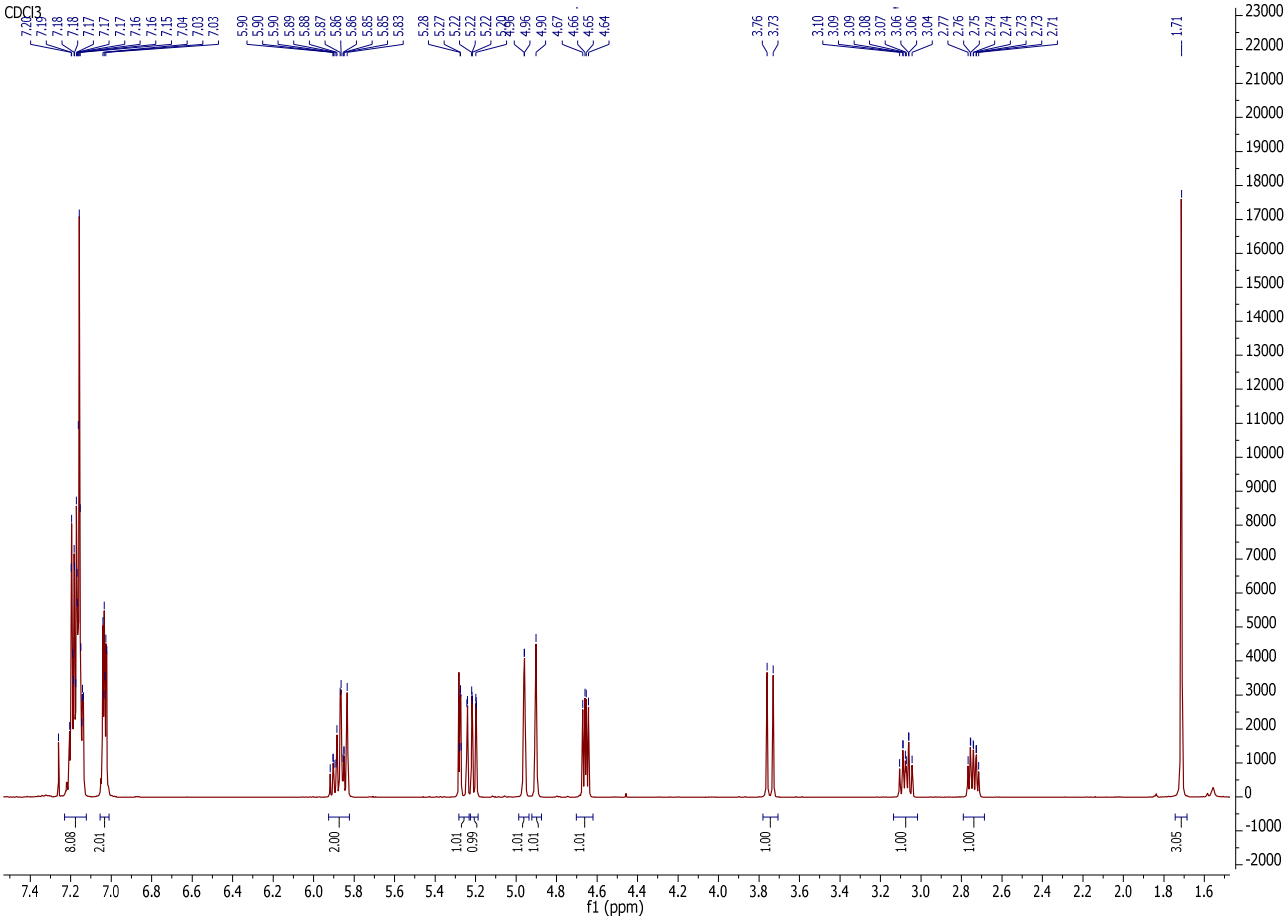

CDCl3
132.81
130.94
129.54
129.02
128.56
128.48
127.60
120.08
119.05
67.21
56.98
34.43
f1 (ppm)

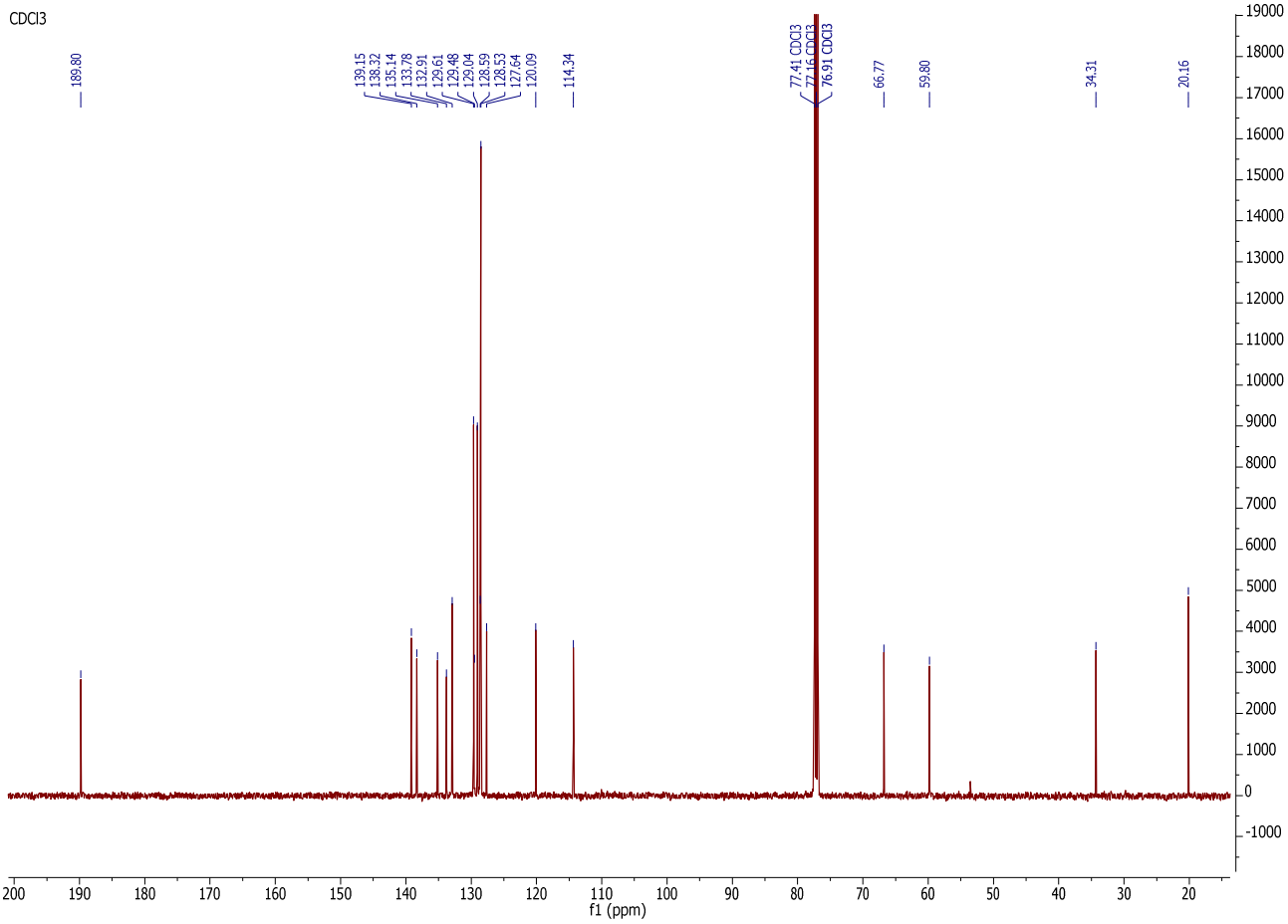

CDCl3
f2 (ppm)
f1 (ppm)

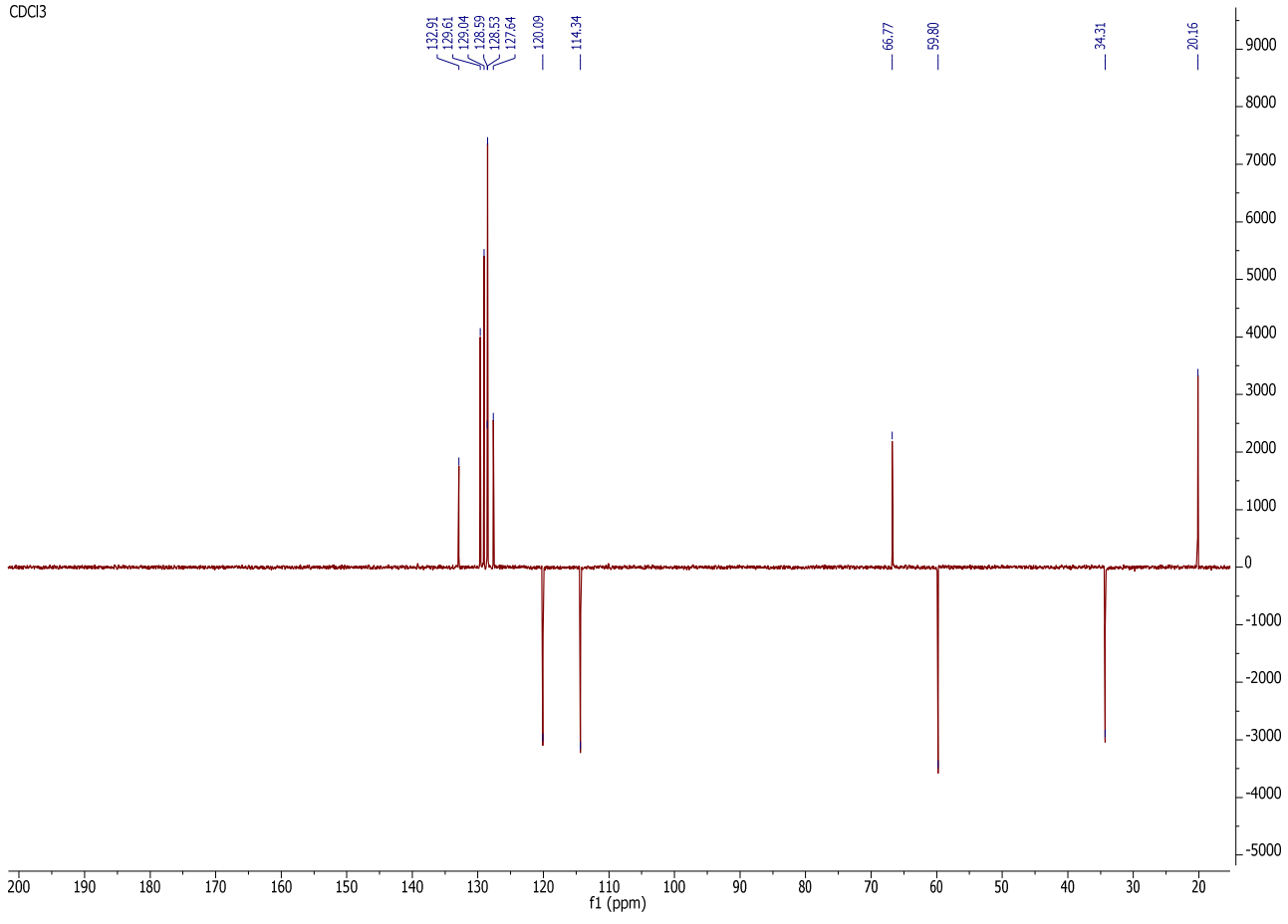

CDCl3
f2 (ppm)
f1 (ppm)

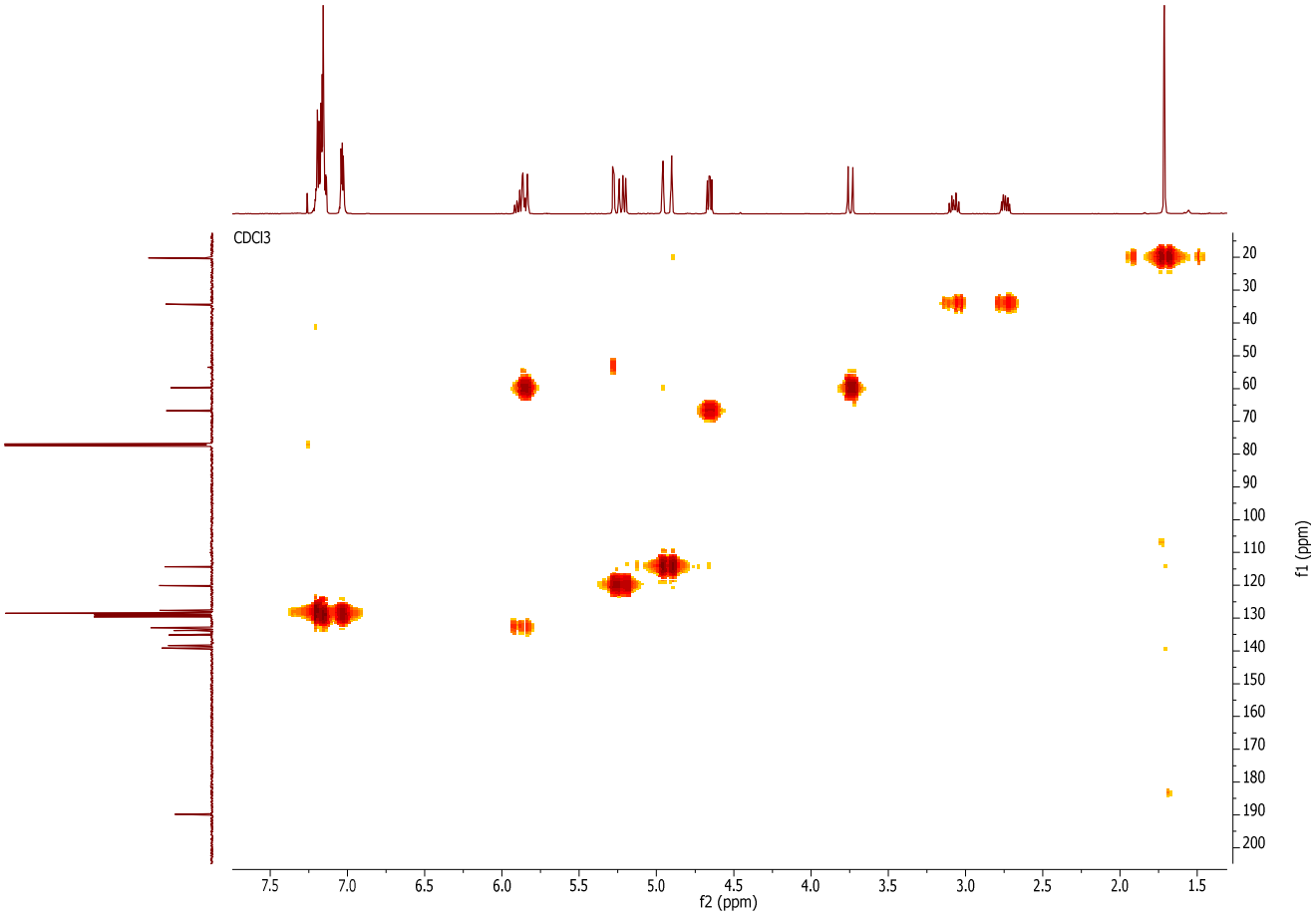


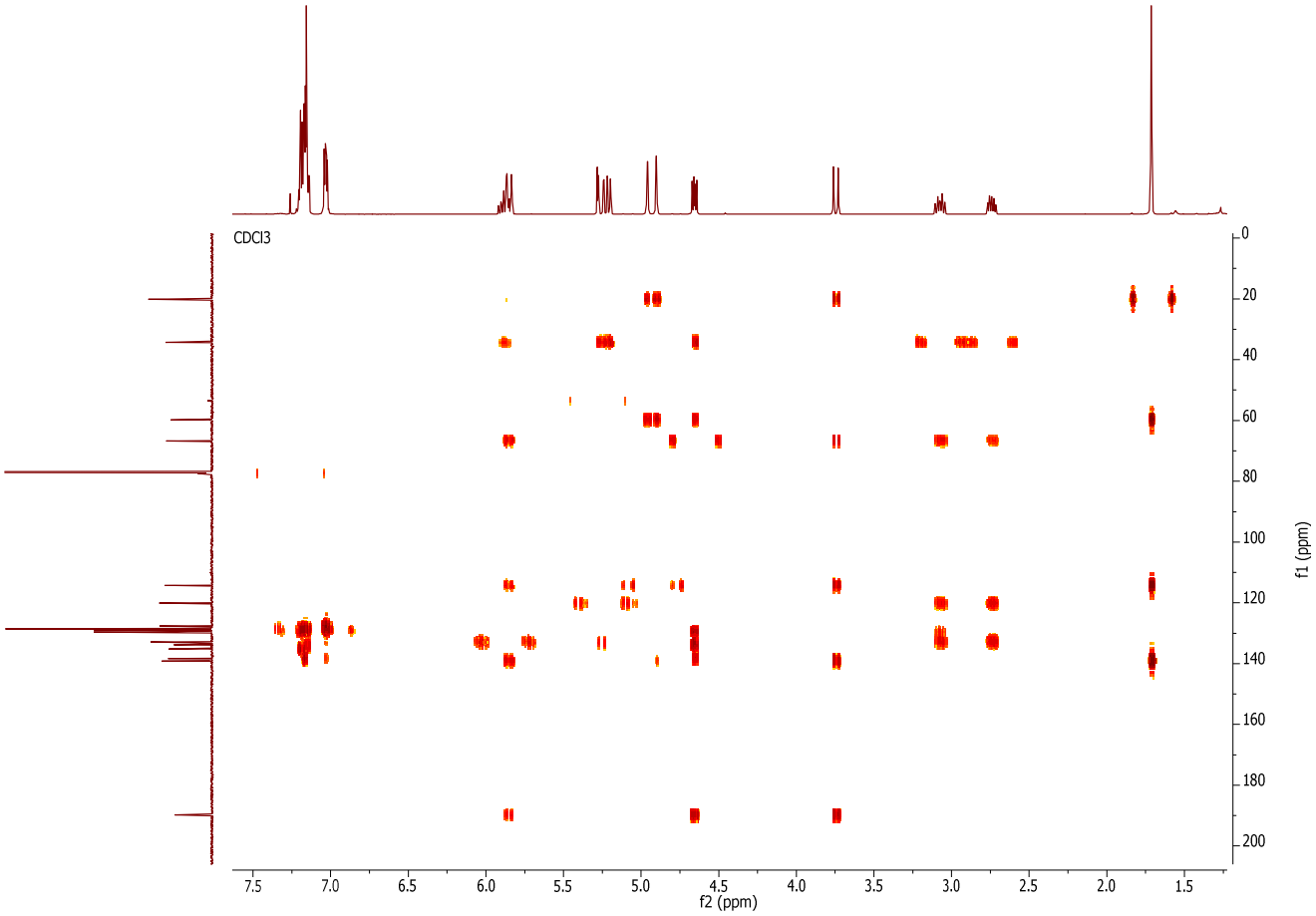
5b

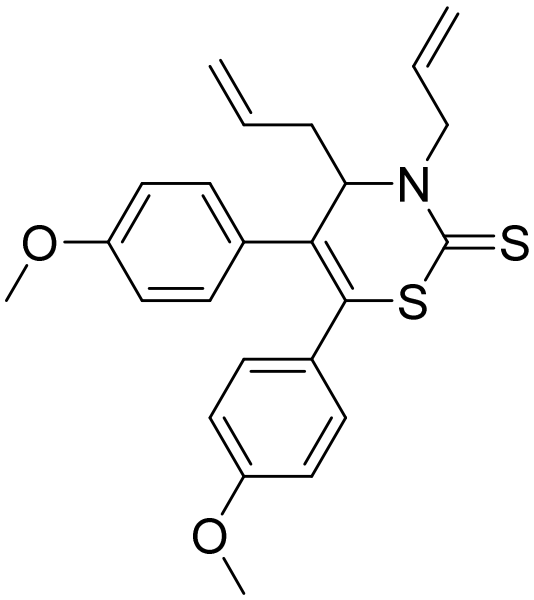



CDCl3
189.80
139.15
138.32
135.14
133.78
132.91
129.61
129.48
129.04
128.59
128.53
127.64
120.09
114.34
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
66.77
59.80
34.31
20.16
f1 (ppm)

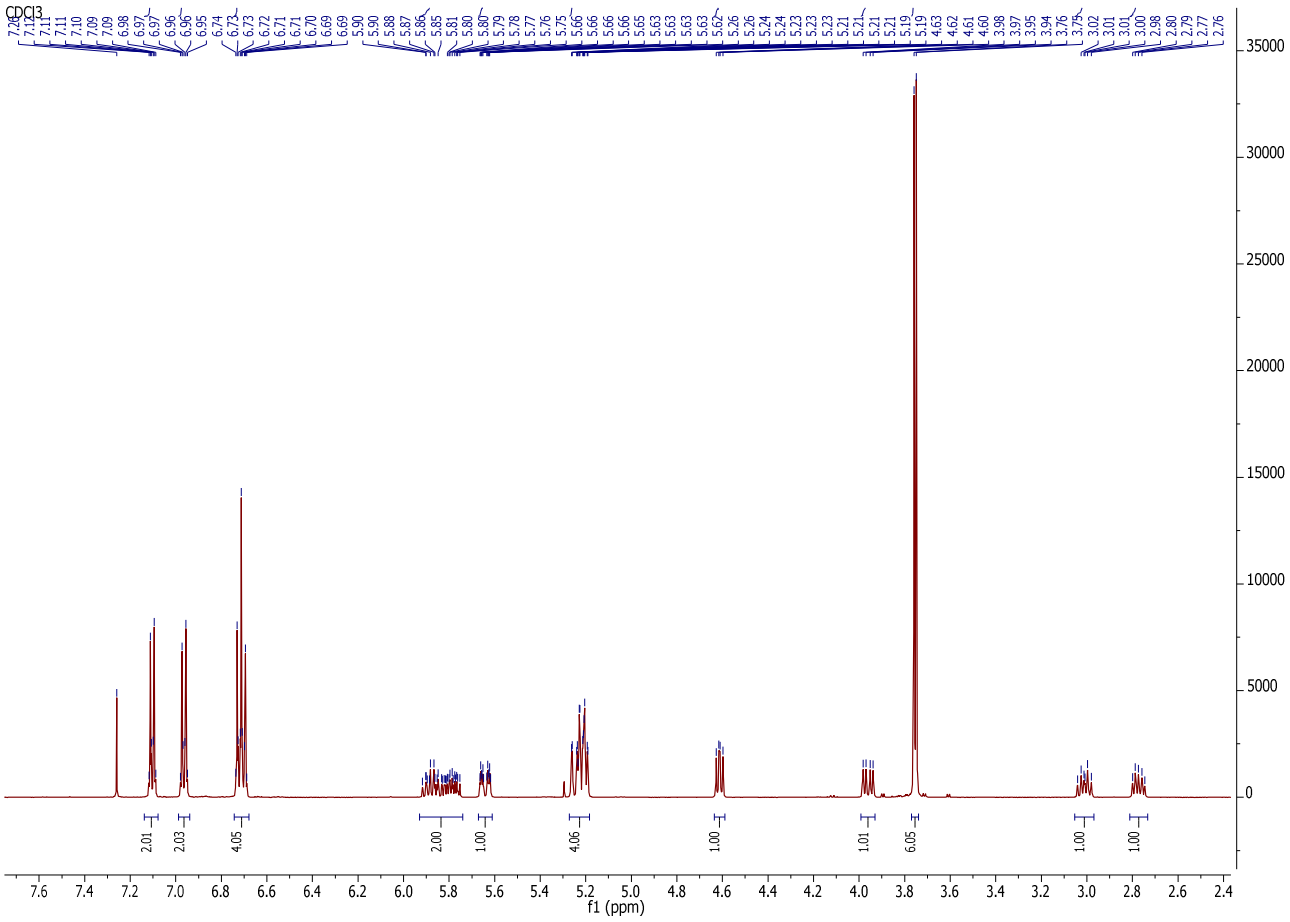

CDCl3
132.91
129.61
129.04
128.59
128.53
127.64
120.09
114.34
66.77
59.80
34.31
20.16
f1 (ppm)

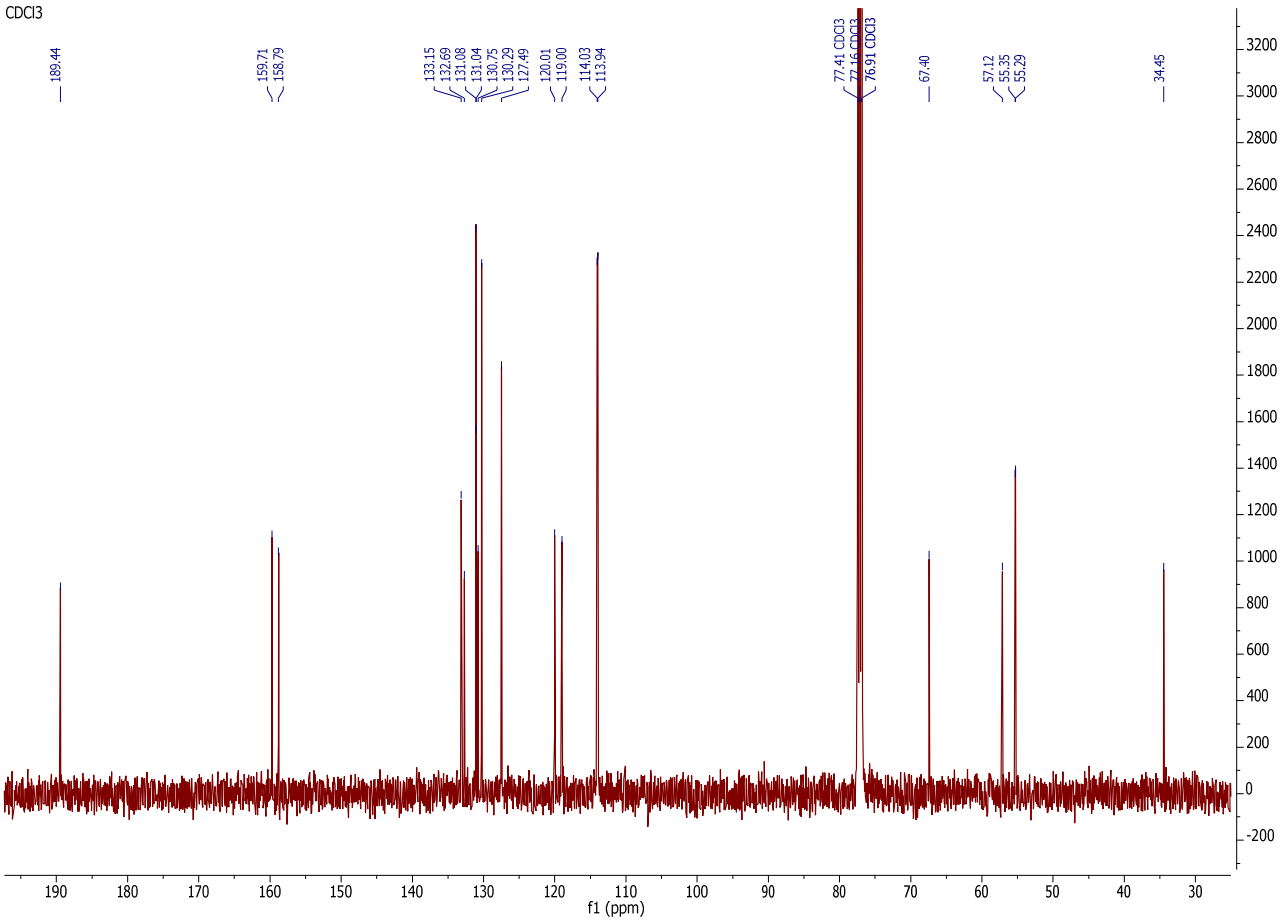

CDCl3
f2 (ppm)
f1 (ppm)

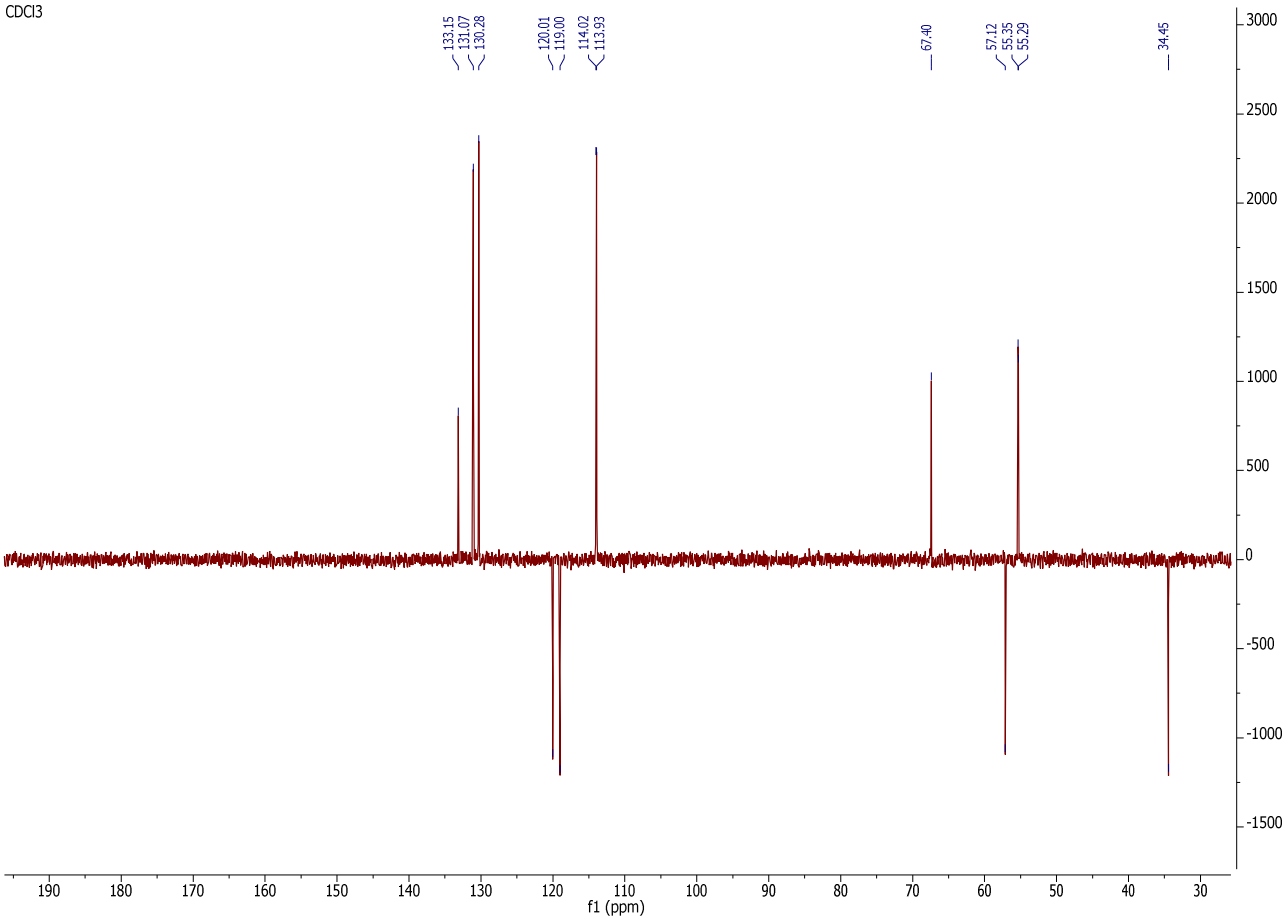

CDCl3
f2 (ppm)
f1 (ppm)

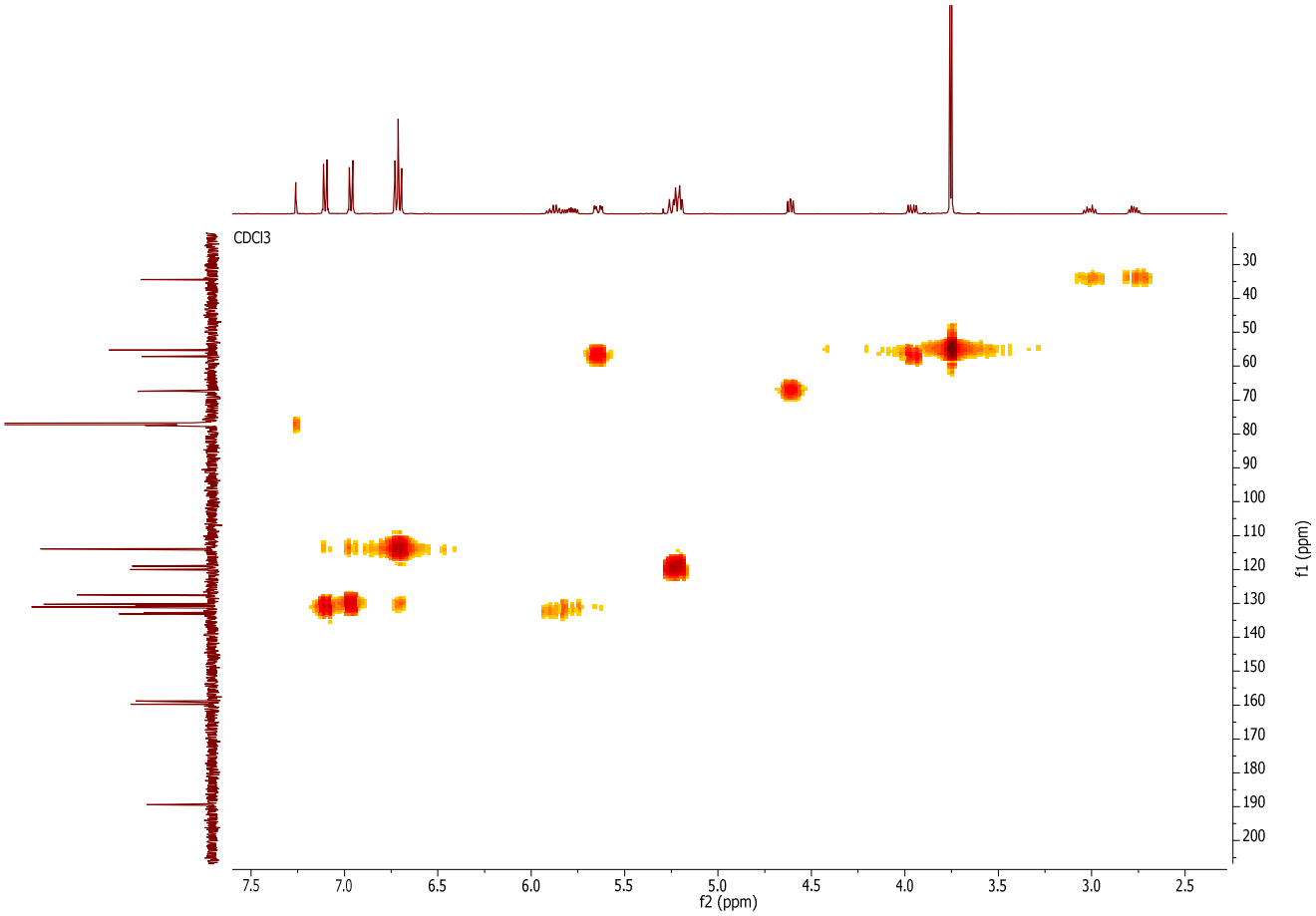


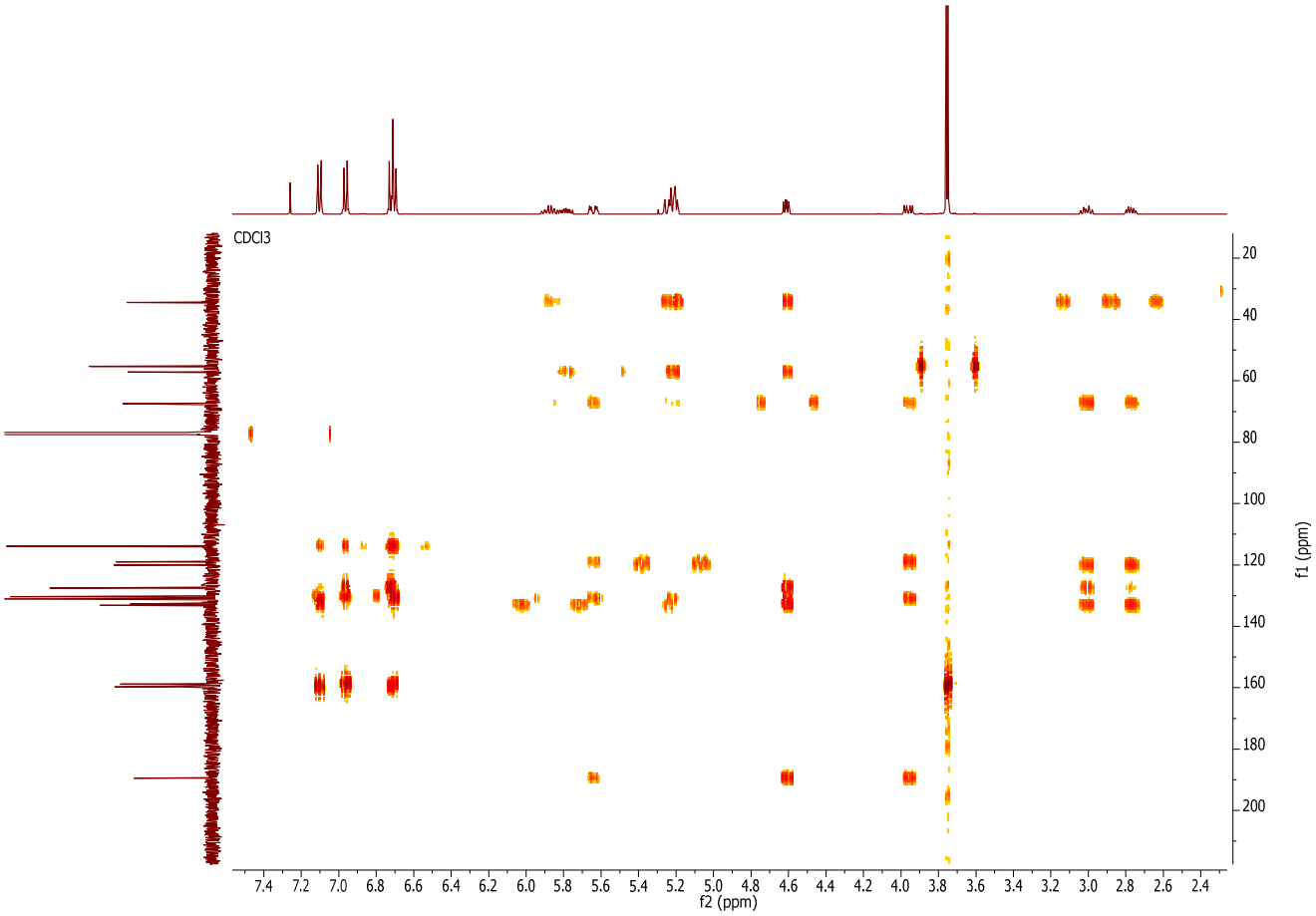
5c

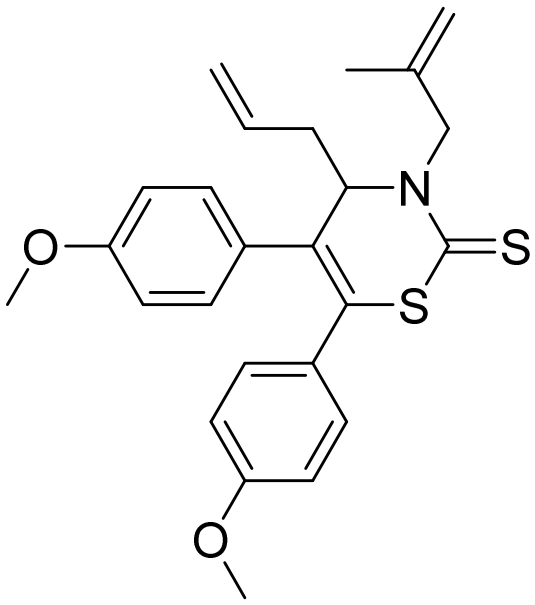



CDCl3
189.44
159.71
158.79
133.15
132.69
131.08
131.04
130.75
130.29
127.49
120.01
119.00
114.03
113.94
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
67.40
57.12
55.35
55.29
34.45
f1 (ppm)

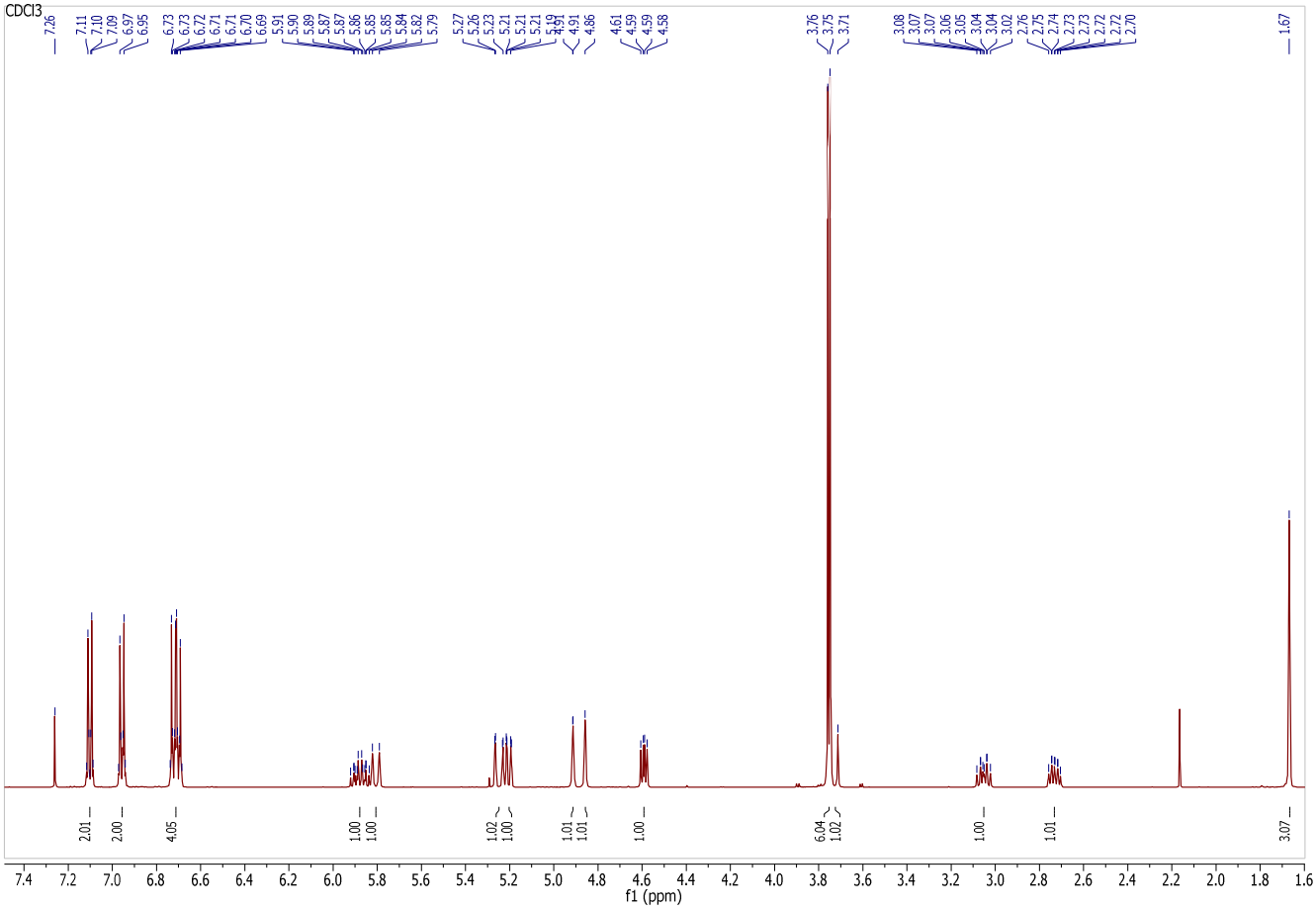

CDCl3
133.15
131.07
130.28
120.01
119.00
114.02
113.93
67.40
57.12
55.35
55.29
34.45
f1 (ppm)

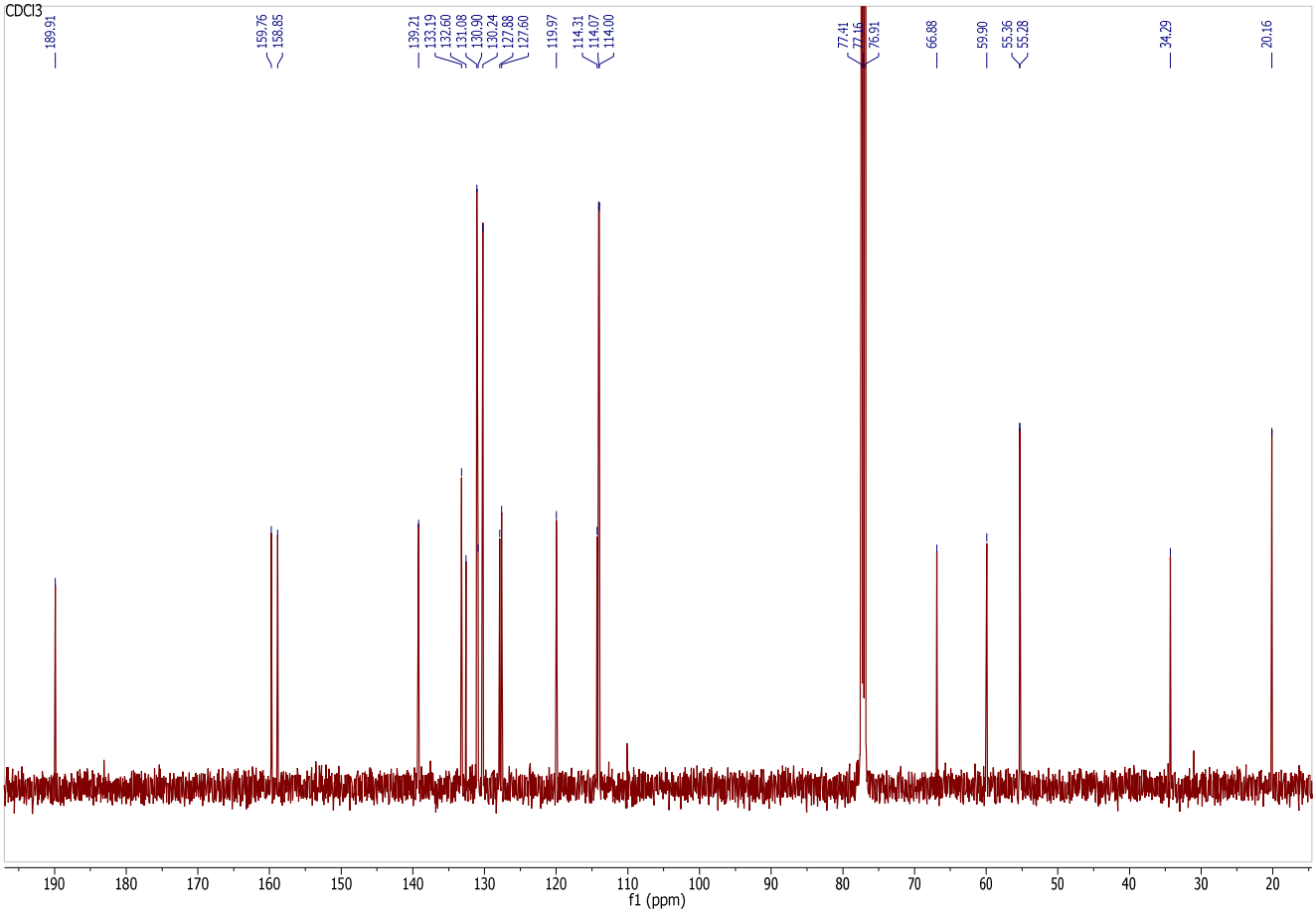

CDCl3
f2 (ppm)
f1 (ppm)

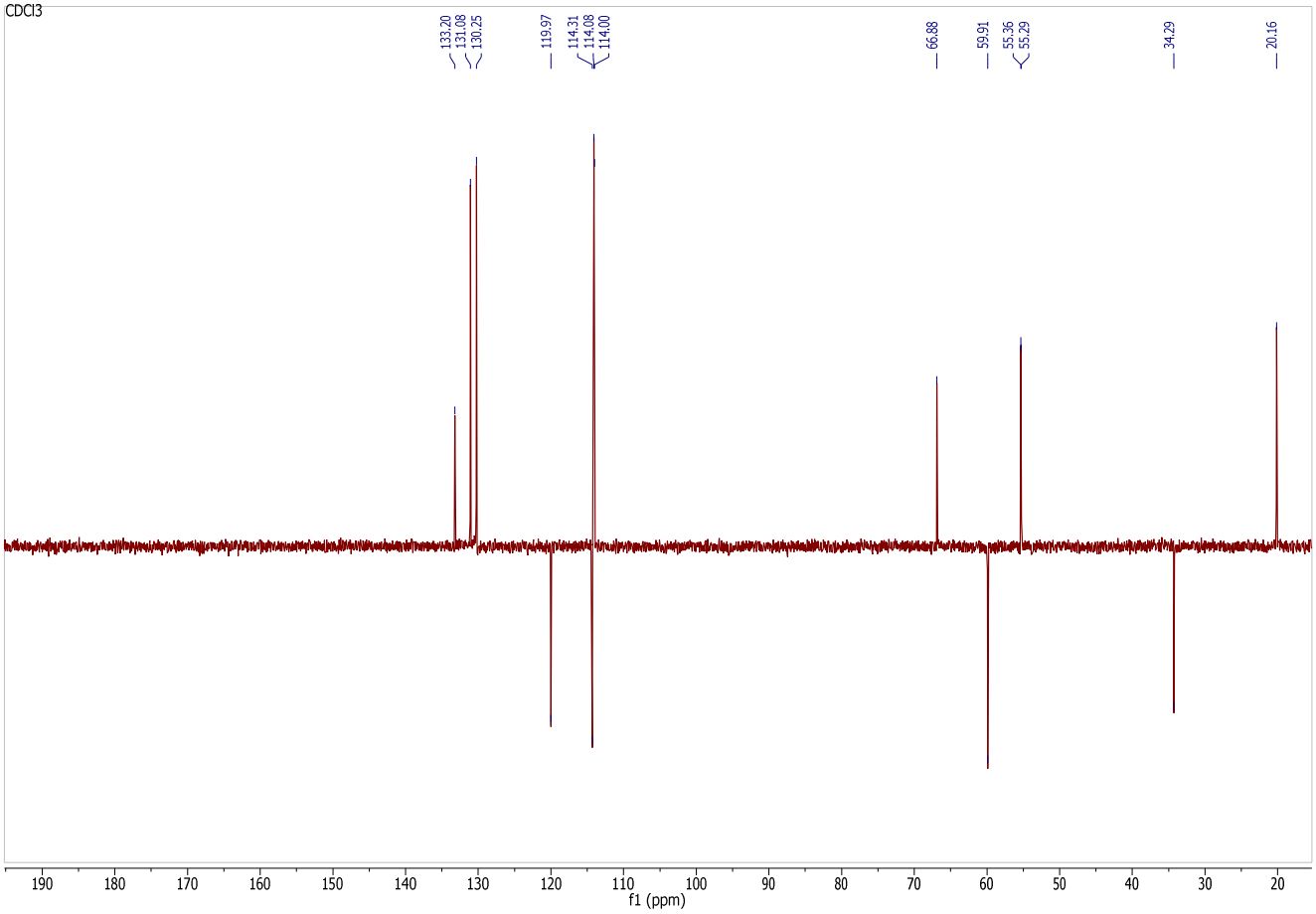

CDCl3
f2 (ppm)
f1 (ppm)



5d




CDCl3
189.91
159.76
158.85
139.21
133.19
132.60
131.08
130.90
130.24
127.88
127.60
119.97
114.31
114.07
114.00
77.41
77.16
76.91
66.88
59.90
55.36
55.28
34.29
20.16
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
f1 (ppm)


CDCl3
133.20
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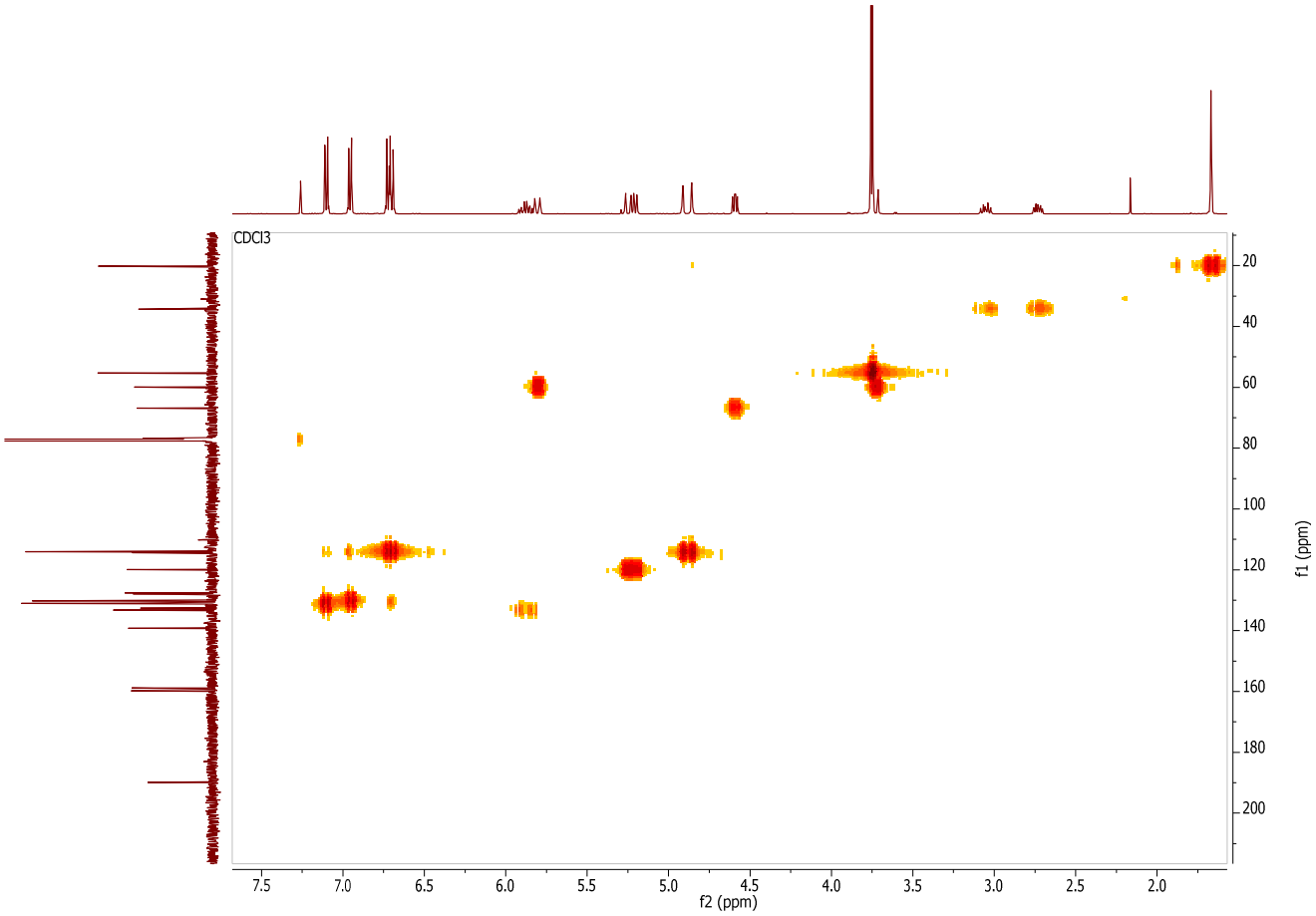
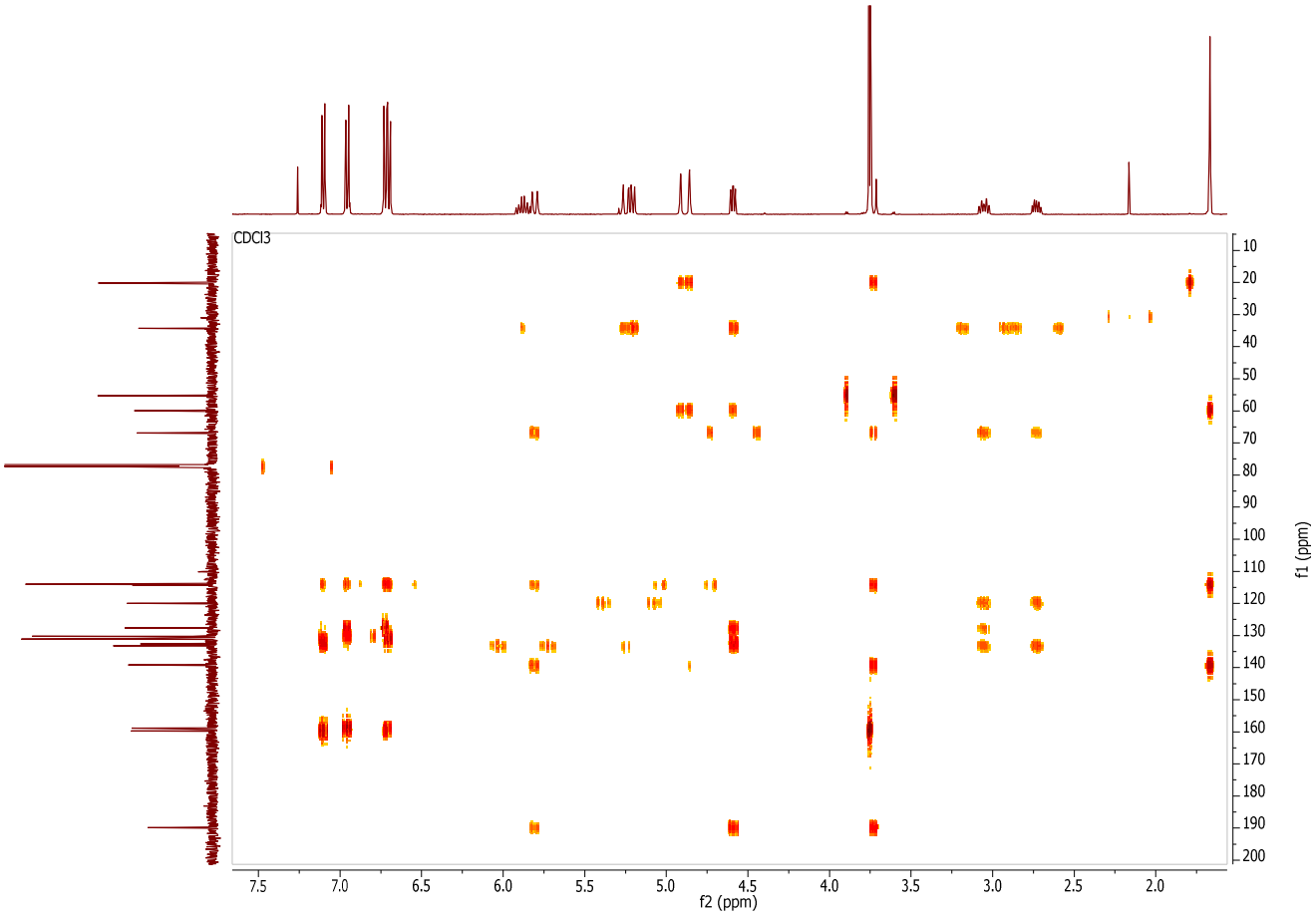
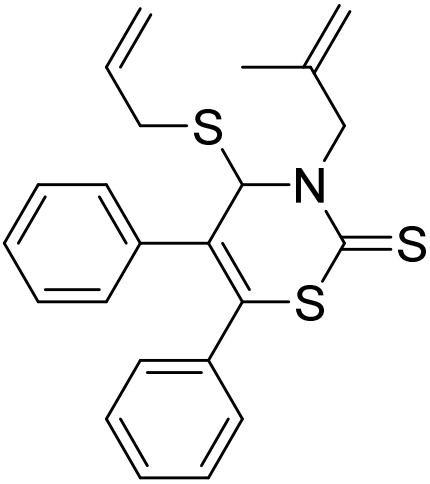
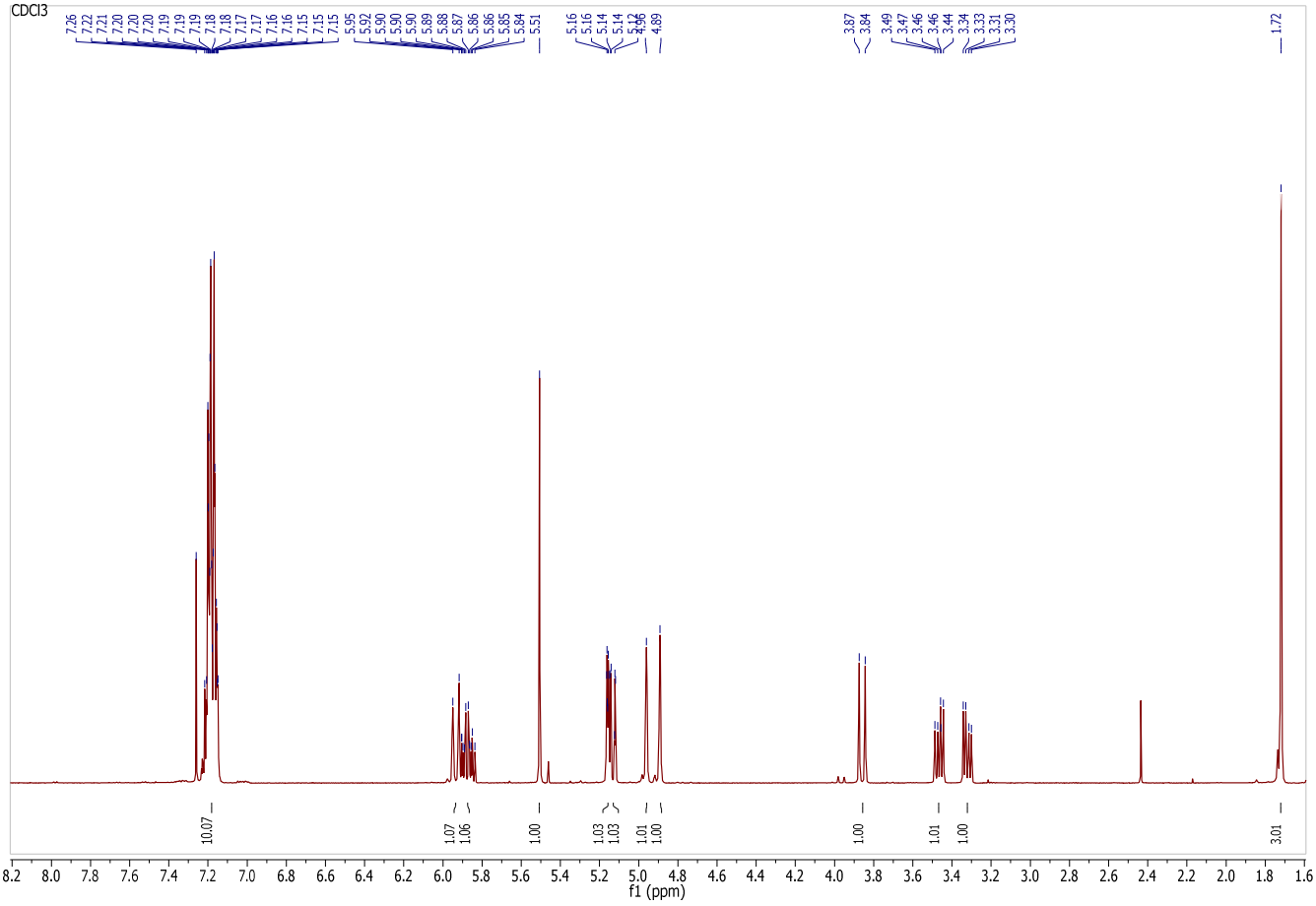
130.25
119.97
114.31
114.08
114.00
66.88
59.91
55.36
55.29
34.29
20.16
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
f1 (ppm)

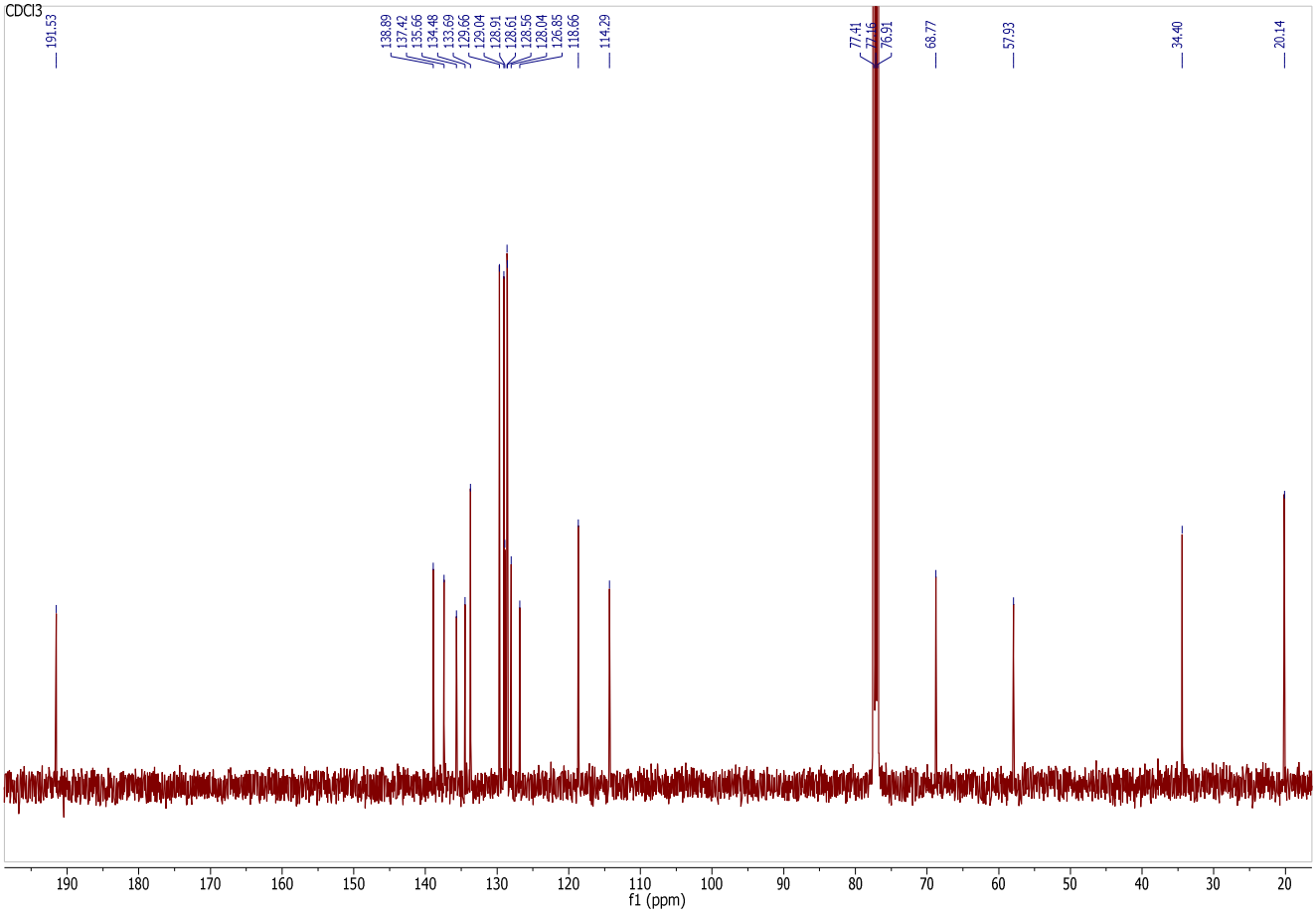

CDCl3
f2 (ppm)
f1 (ppm)

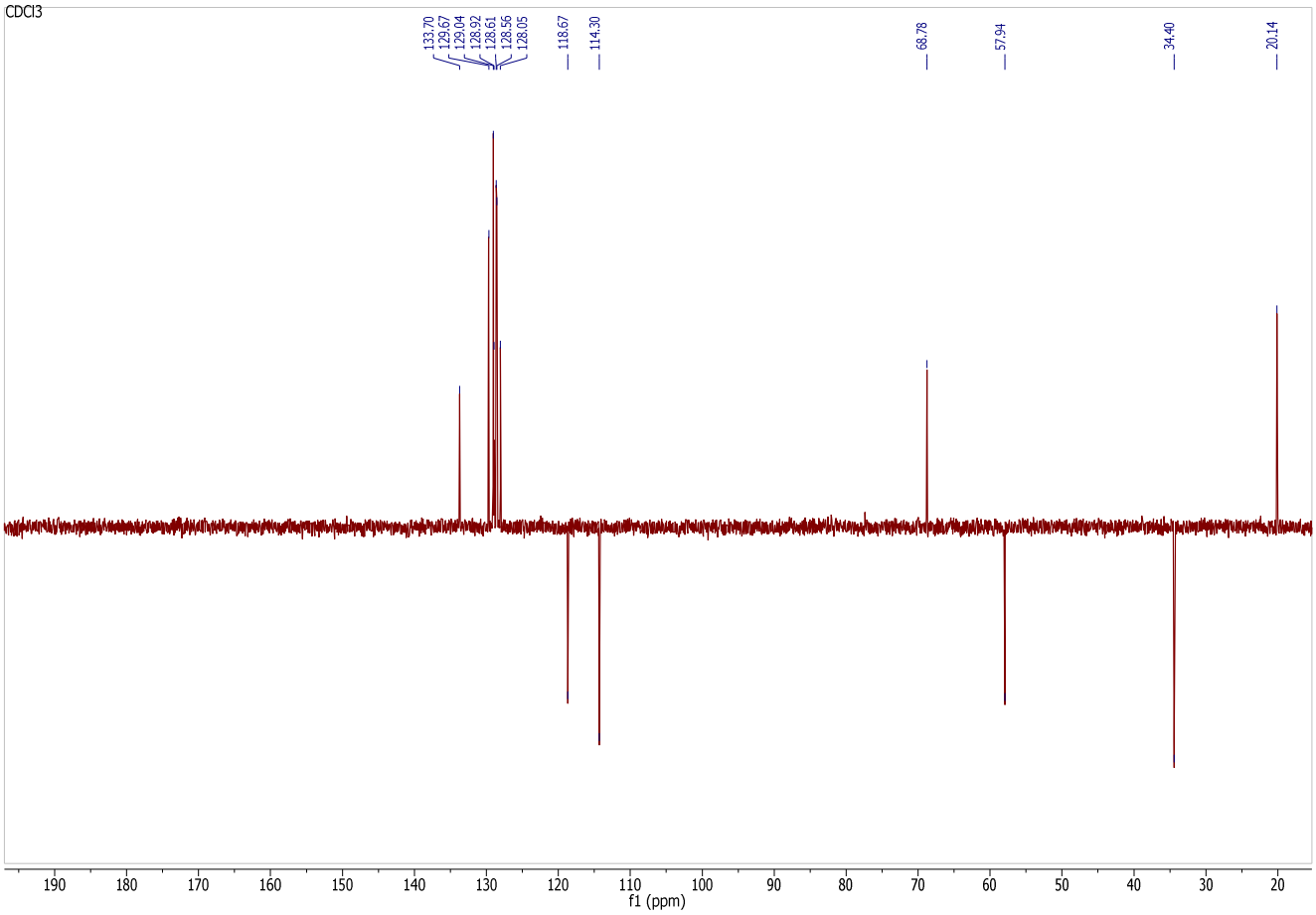

CDCl3
f2 (ppm)
f1 (ppm)

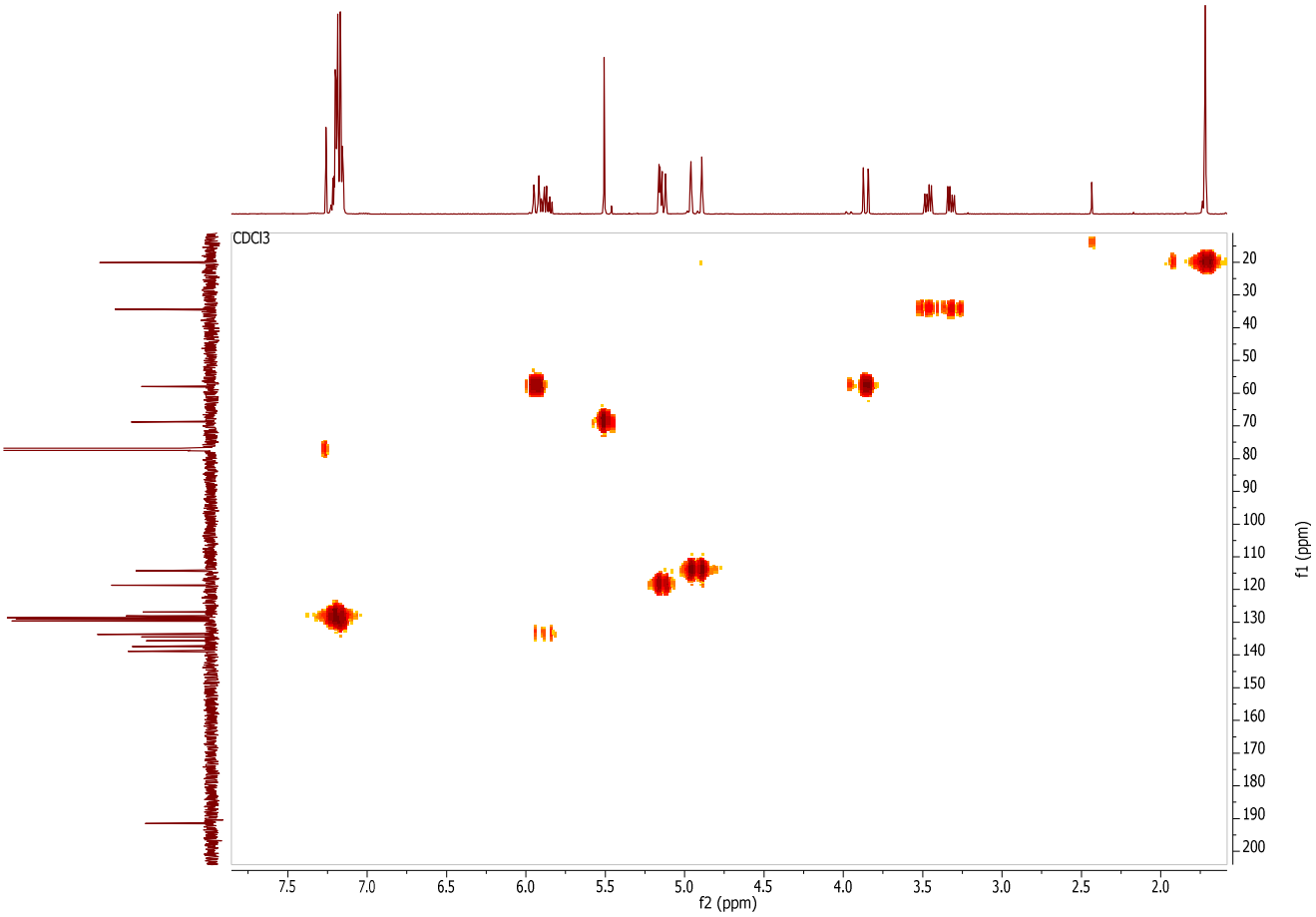


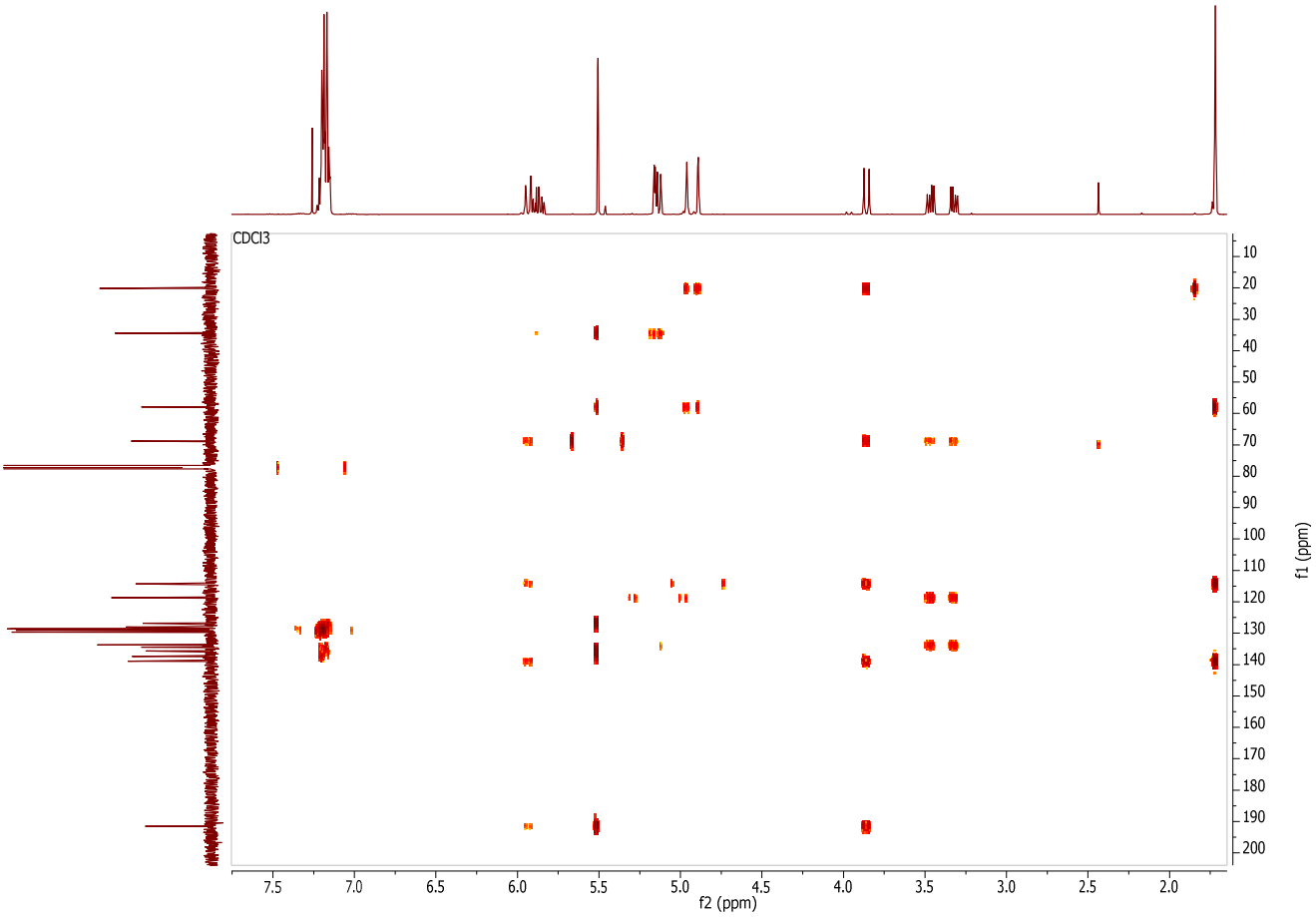
5e

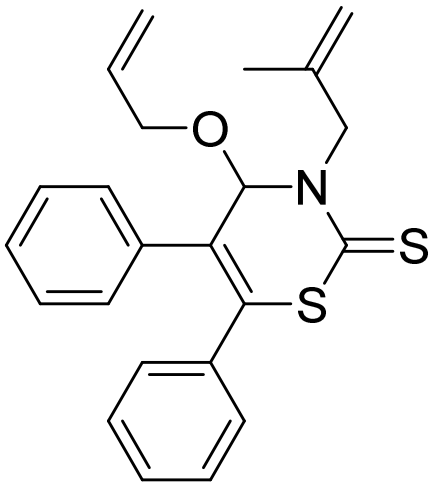



CDCl3
191.53
138.89
137.42
135.66
134.48
133.69
129.66
129.04
128.91
128.61
128.56
128.04
126.85
118.66
114.29
77.41
77.16
76.91
68.77
57.93
34.40
20.14
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

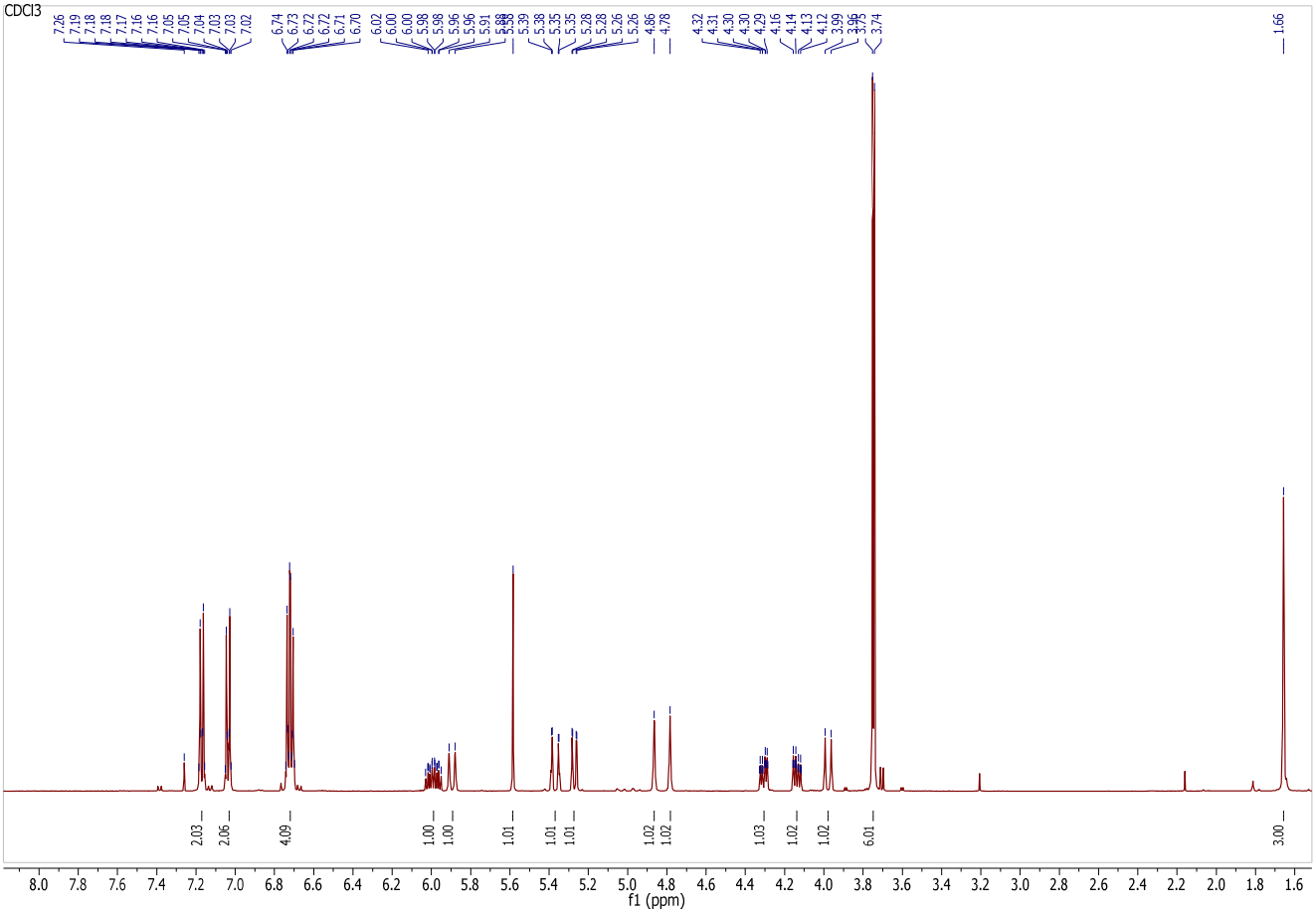

CDCl3
133.70
129.67
129.04
128.92
128.61
128.56
128.05
118.67
114.30
68.78
57.94
34.40
20.14
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

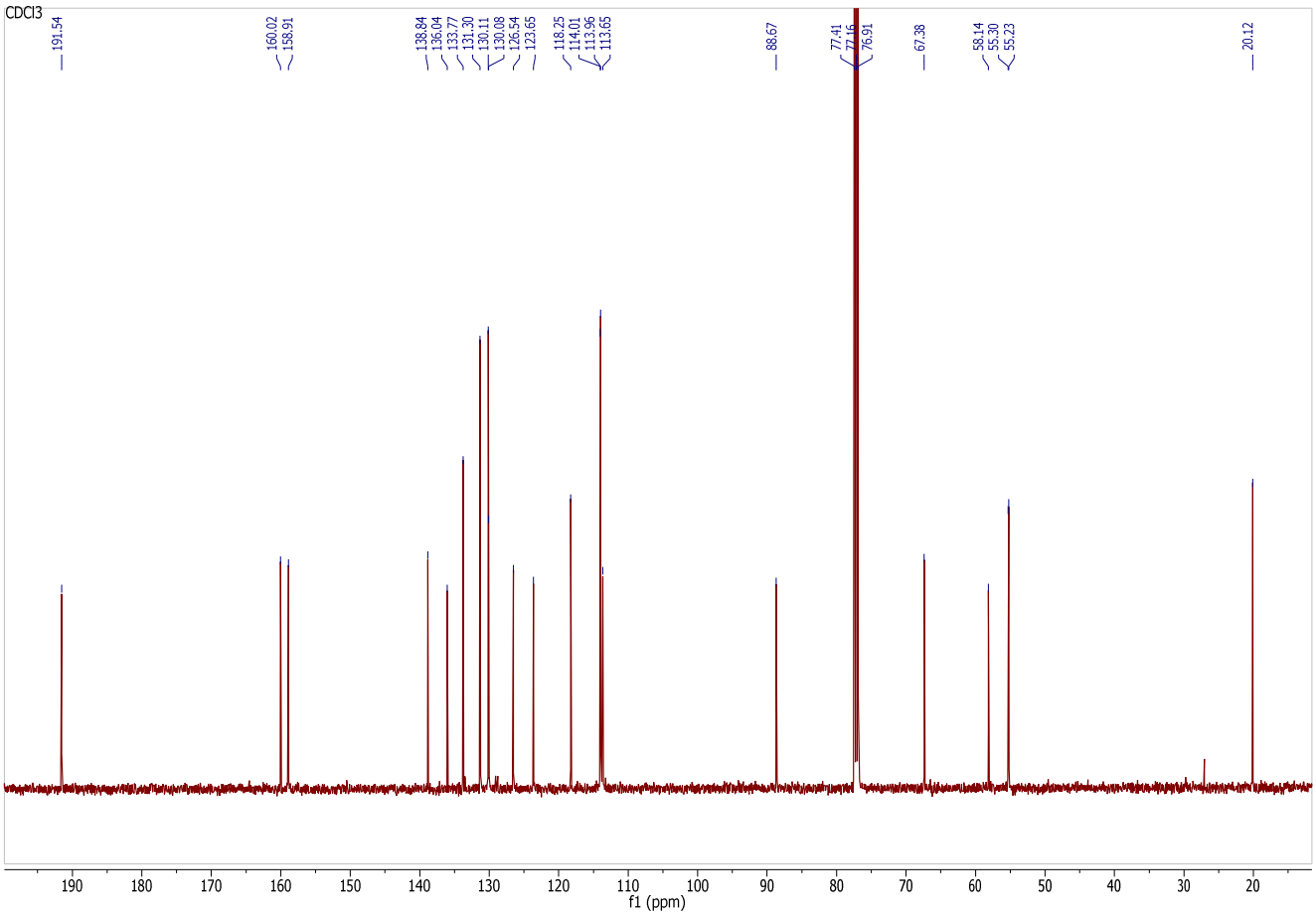

CDCl3
f2 (ppm)
f1 (ppm)

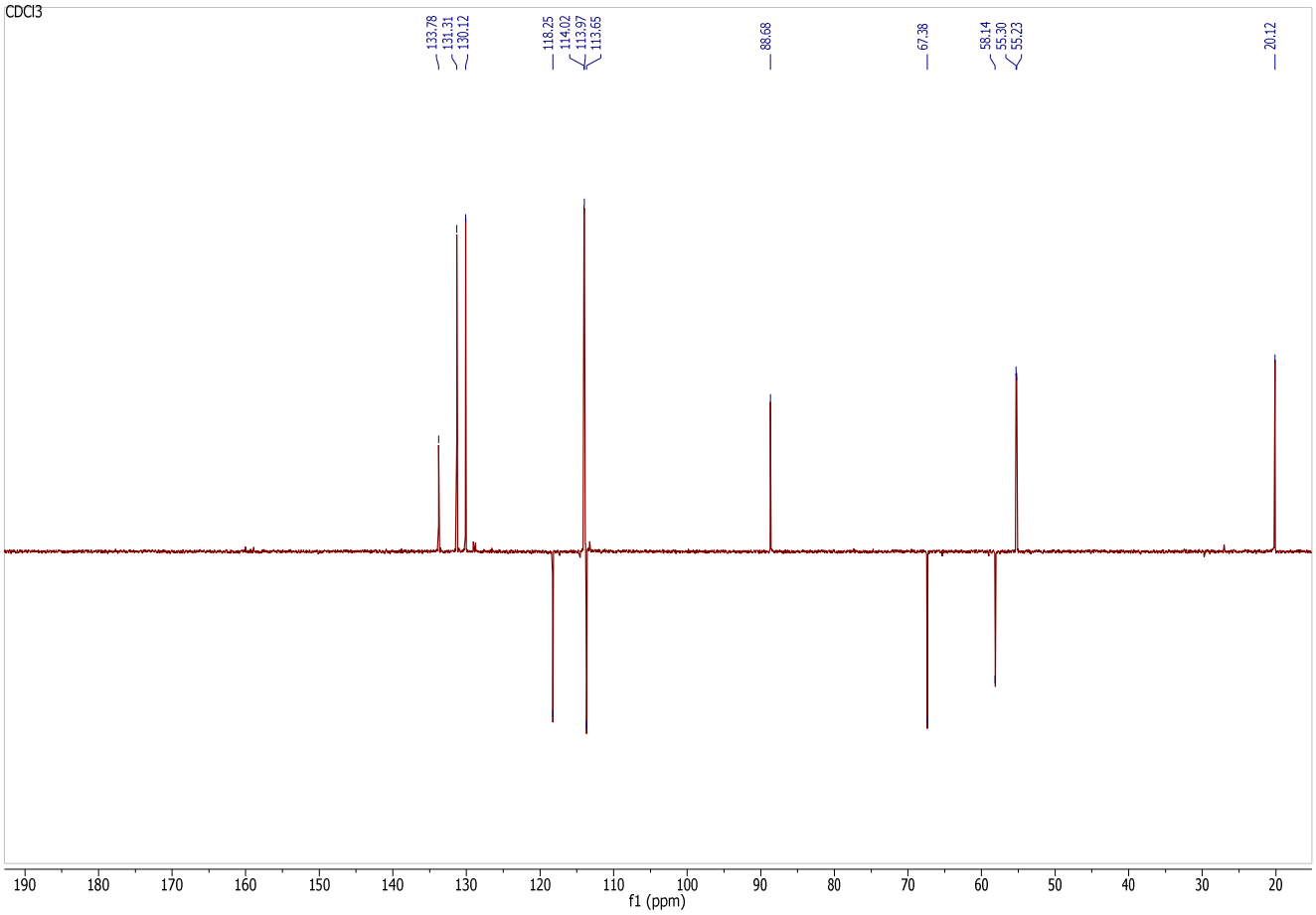

CDCl3
f2 (ppm)
f1 (ppm)

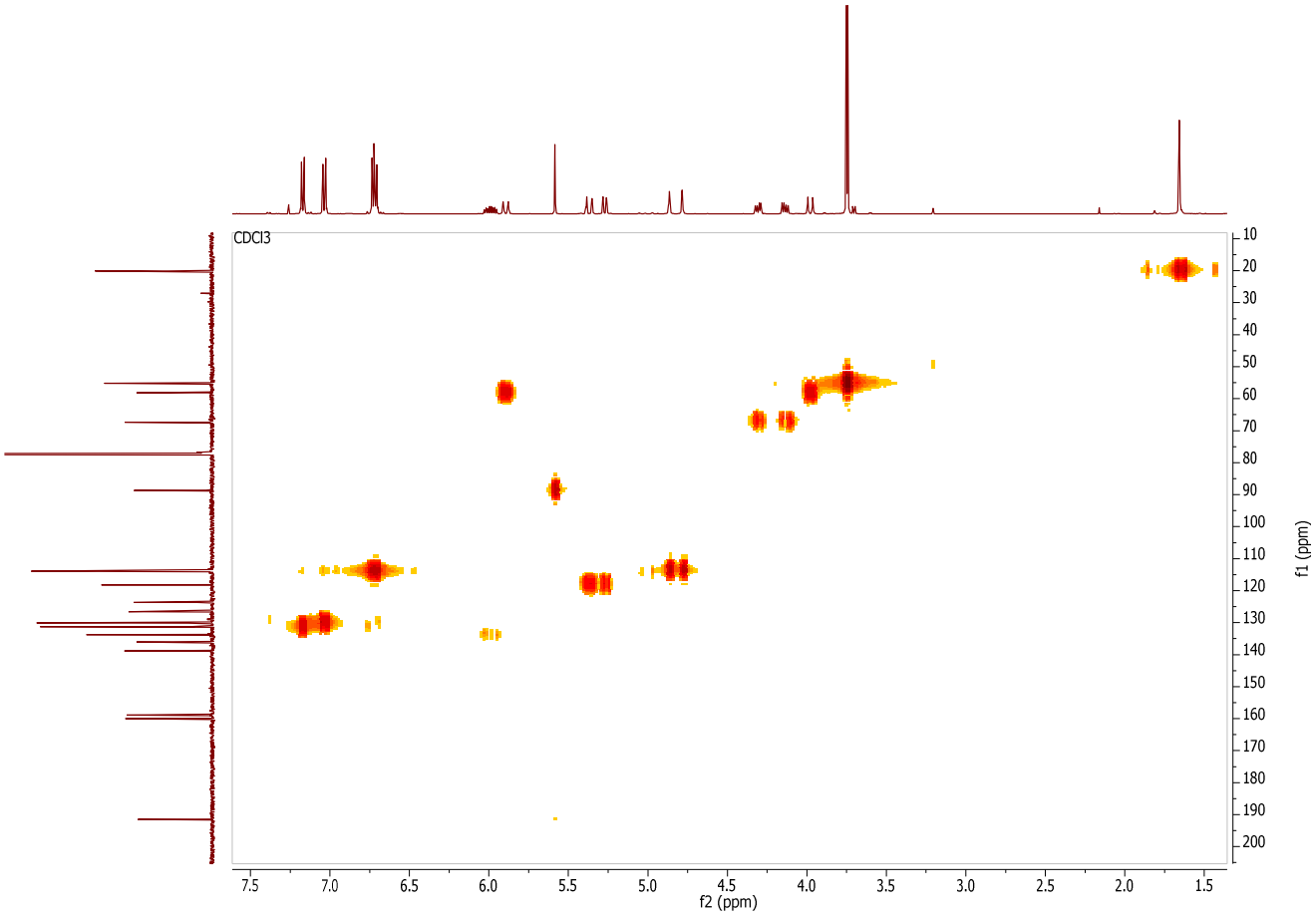


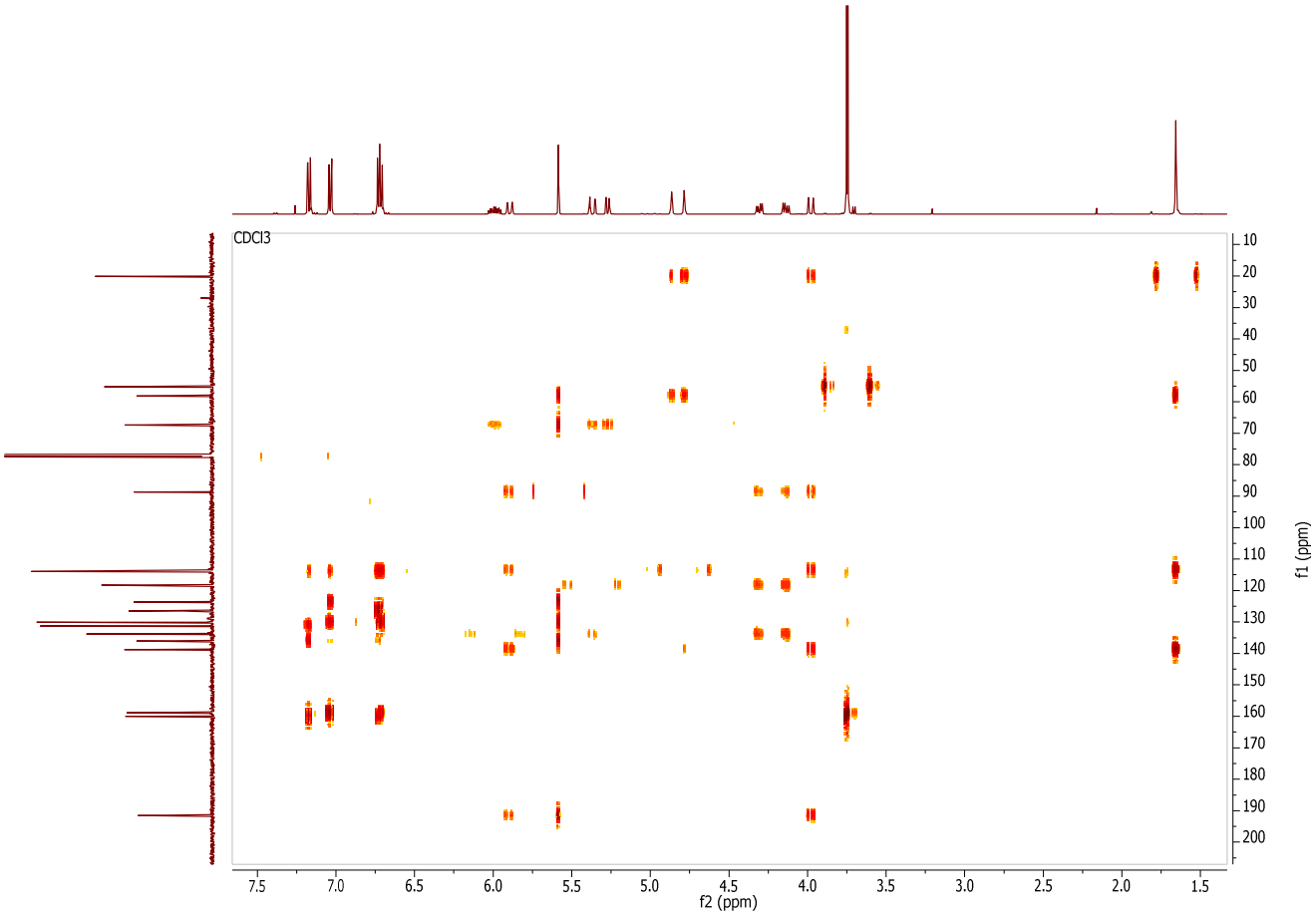
5f

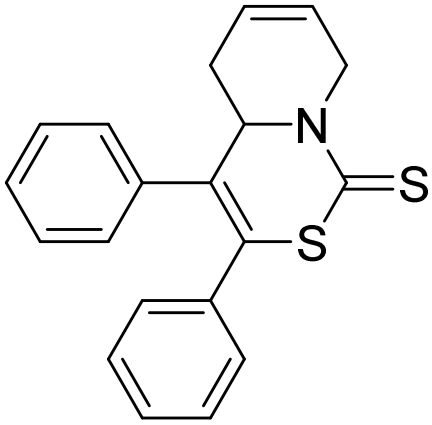



CDCl3
191.54
160.02
158.91
138.84
136.04
133.77
131.30
130.11
130.08
126.54
123.65
118.25
114.01
113.96
113.65
88.67
77.41
77.16
76.91
67.38
58.14
55.30
55.23
20.12
f1 (ppm)

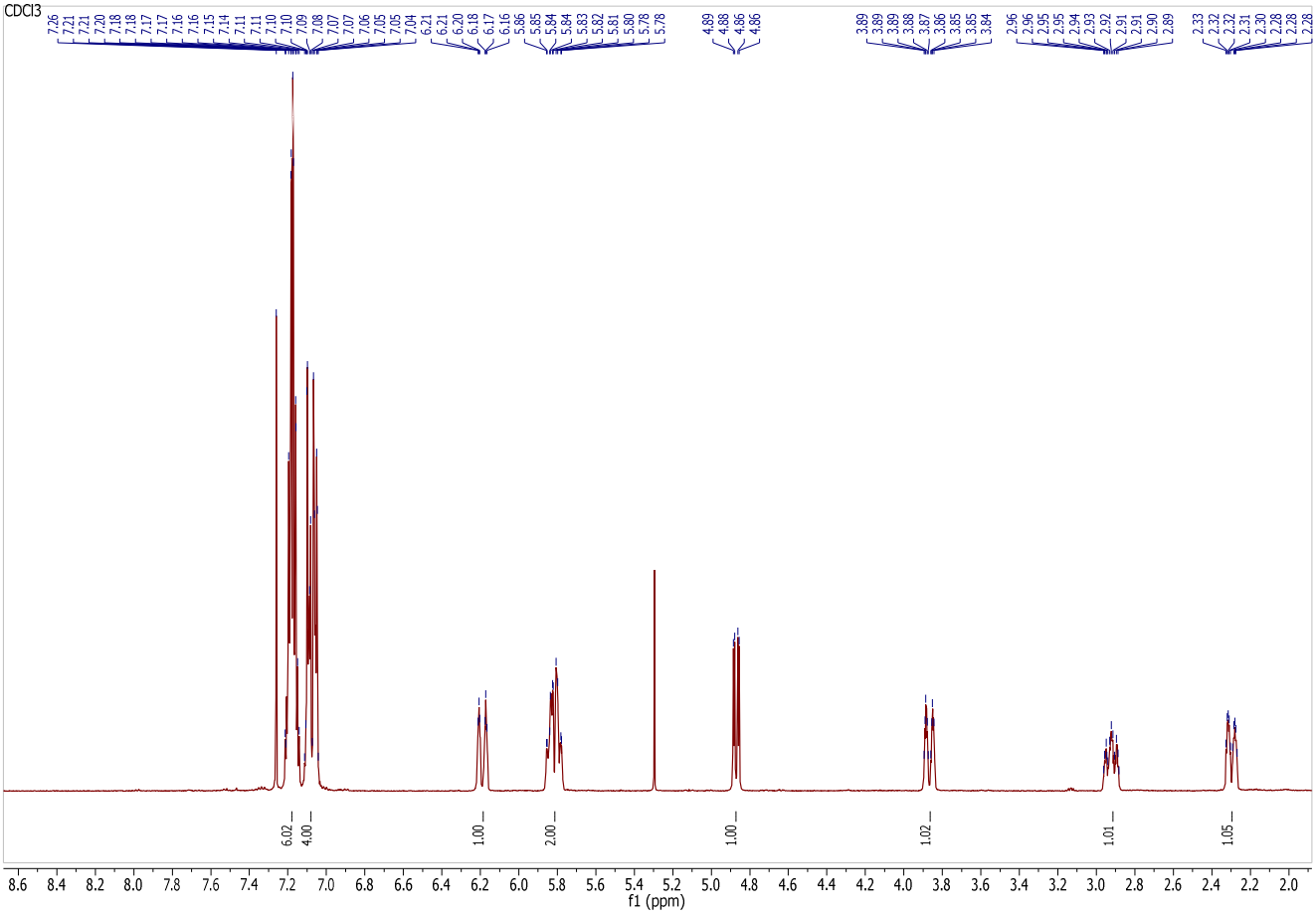

CDCl3
133.78
131.31
130.12
118.25
114.02
113.97
113.65
88.68
67.38
58.14
55.30
55.23
20.12
f1 (ppm)

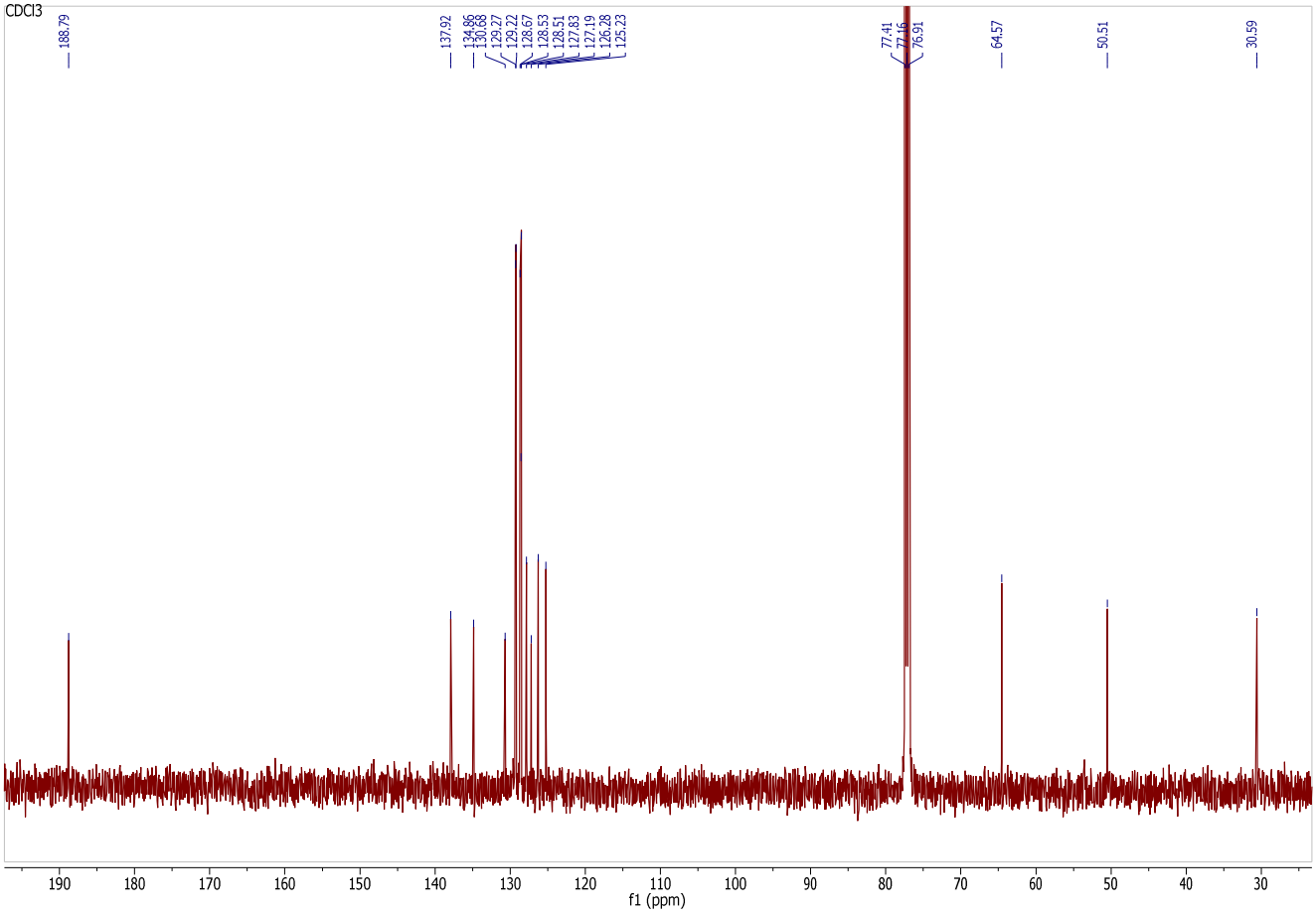

CDCl3
f2 (ppm)
f1 (ppm)

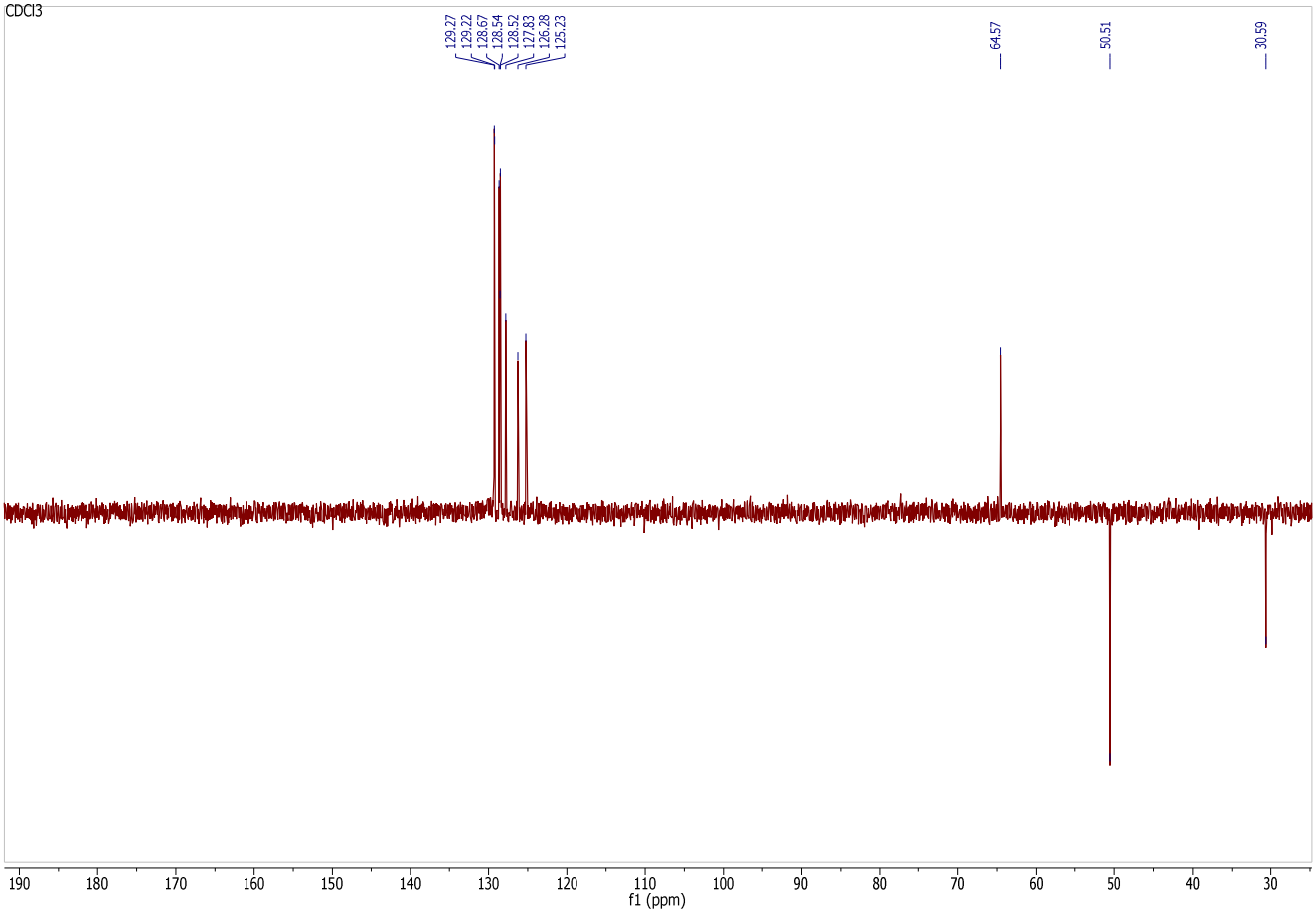

CDCl3
f2 (ppm)
f1 (ppm)

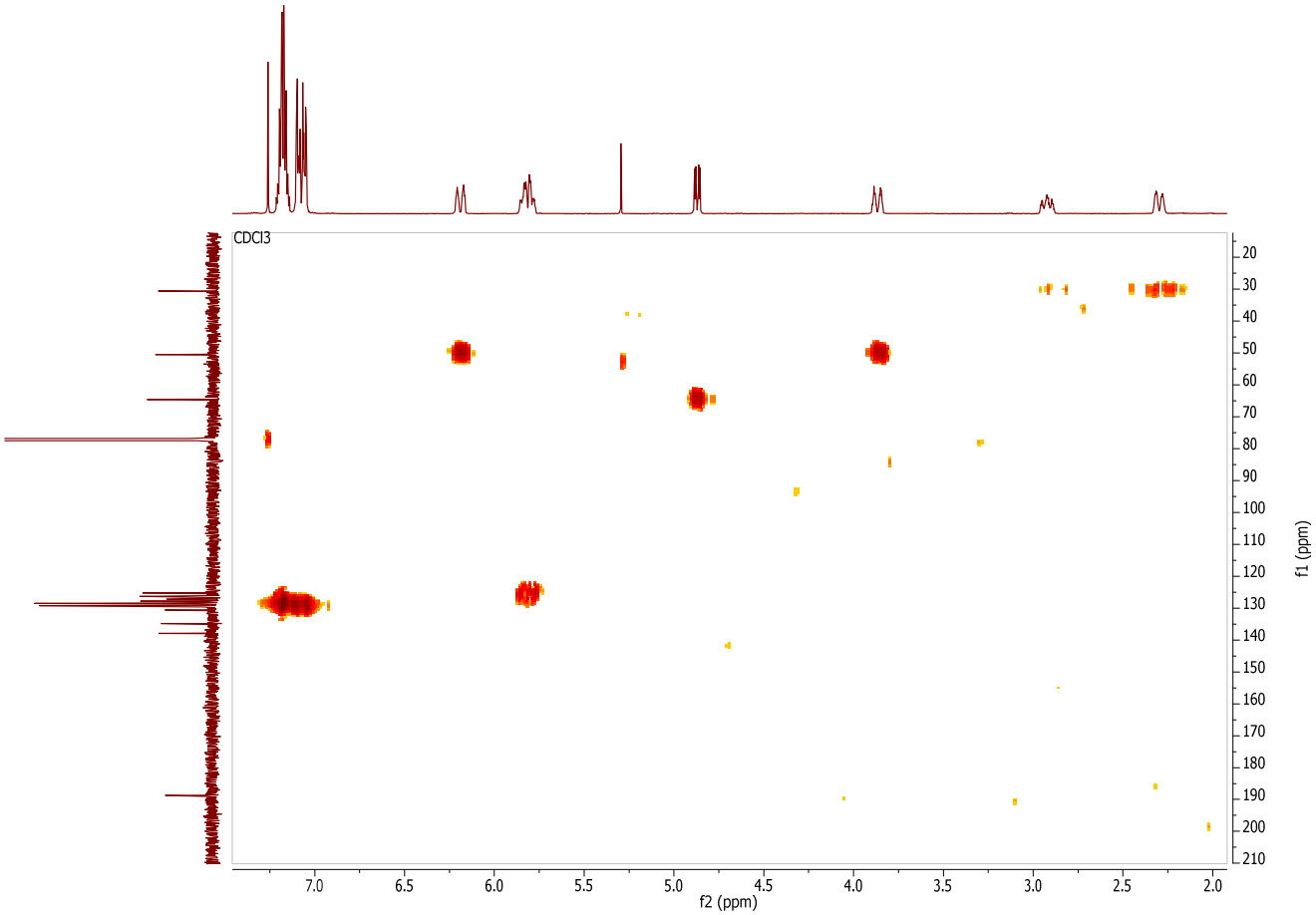


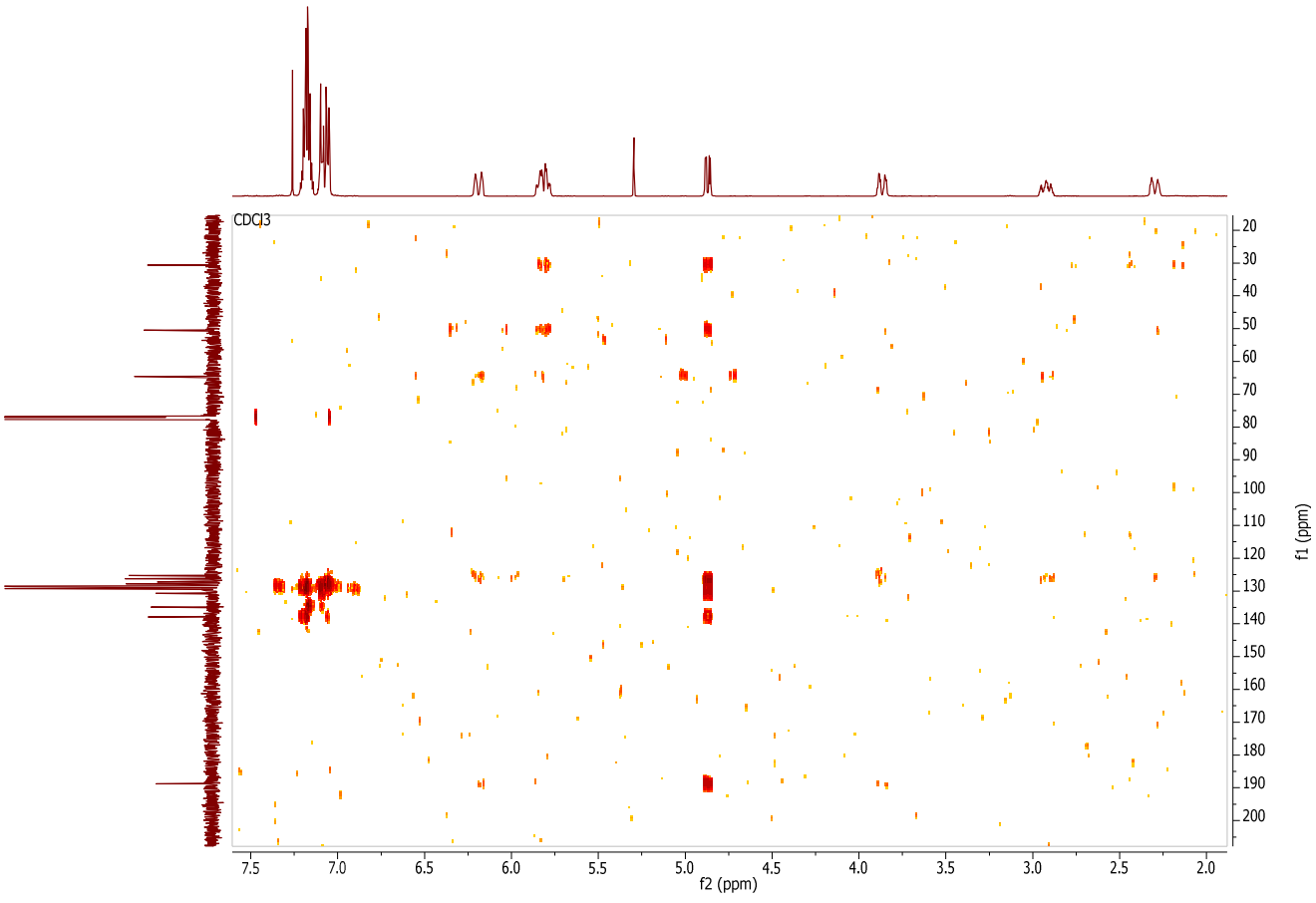
6a

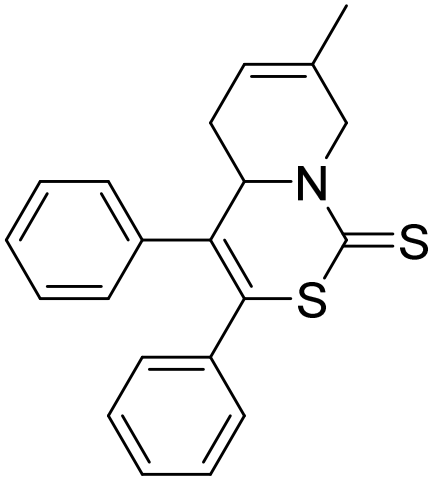



CDCl3
188.79
137.92
134.86
130.68
129.27
129.22
128.67
128.53
128.51
127.83
127.19
126.28
125.23
77.41
77.16
76.91
64.57
50.51
30.59
f1 (ppm)

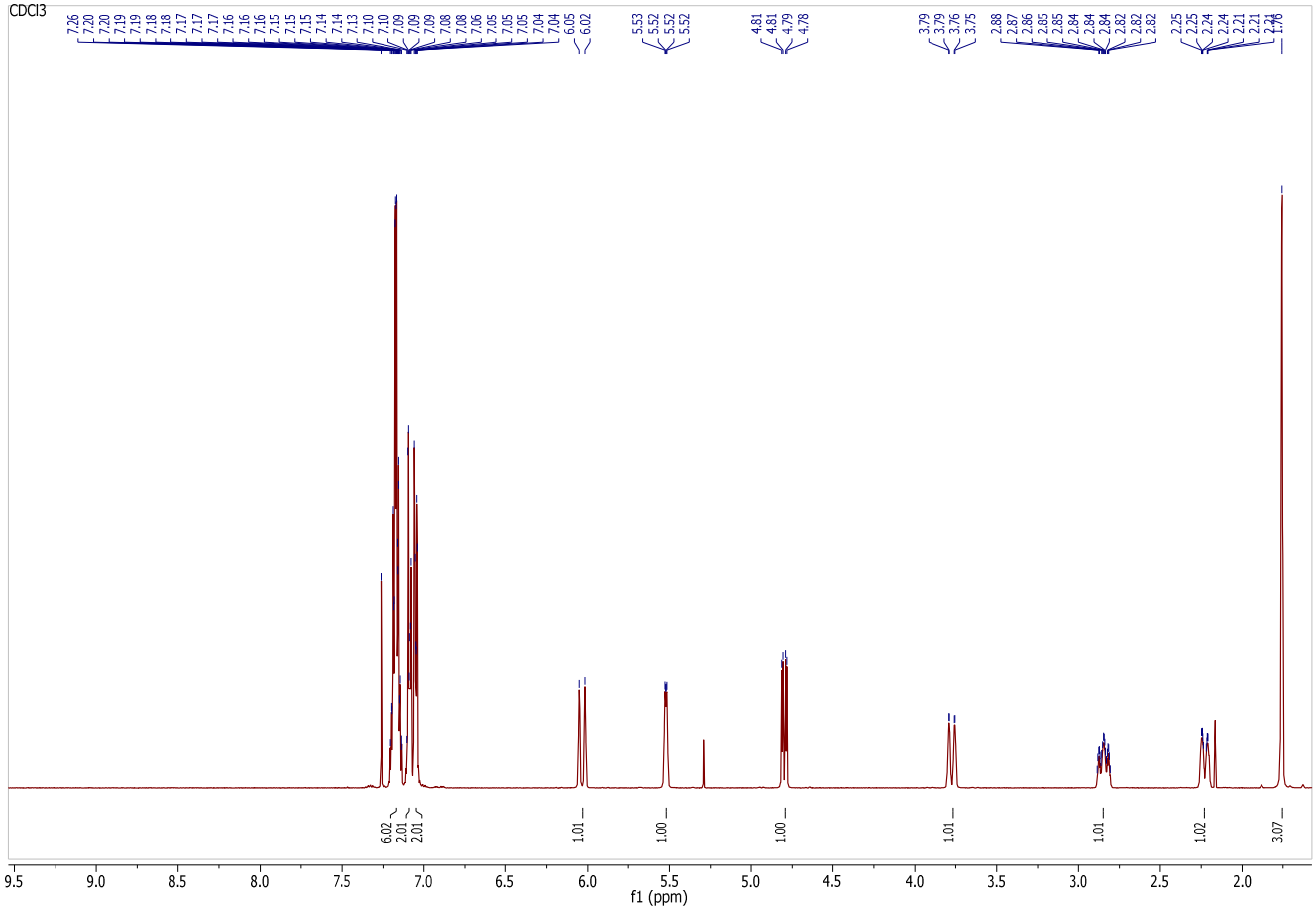

CDCl3
129.27
129.22
128.67
128.54
128.52
127.83
126.28
125.23
64.57
50.51
30.59
f1 (ppm)

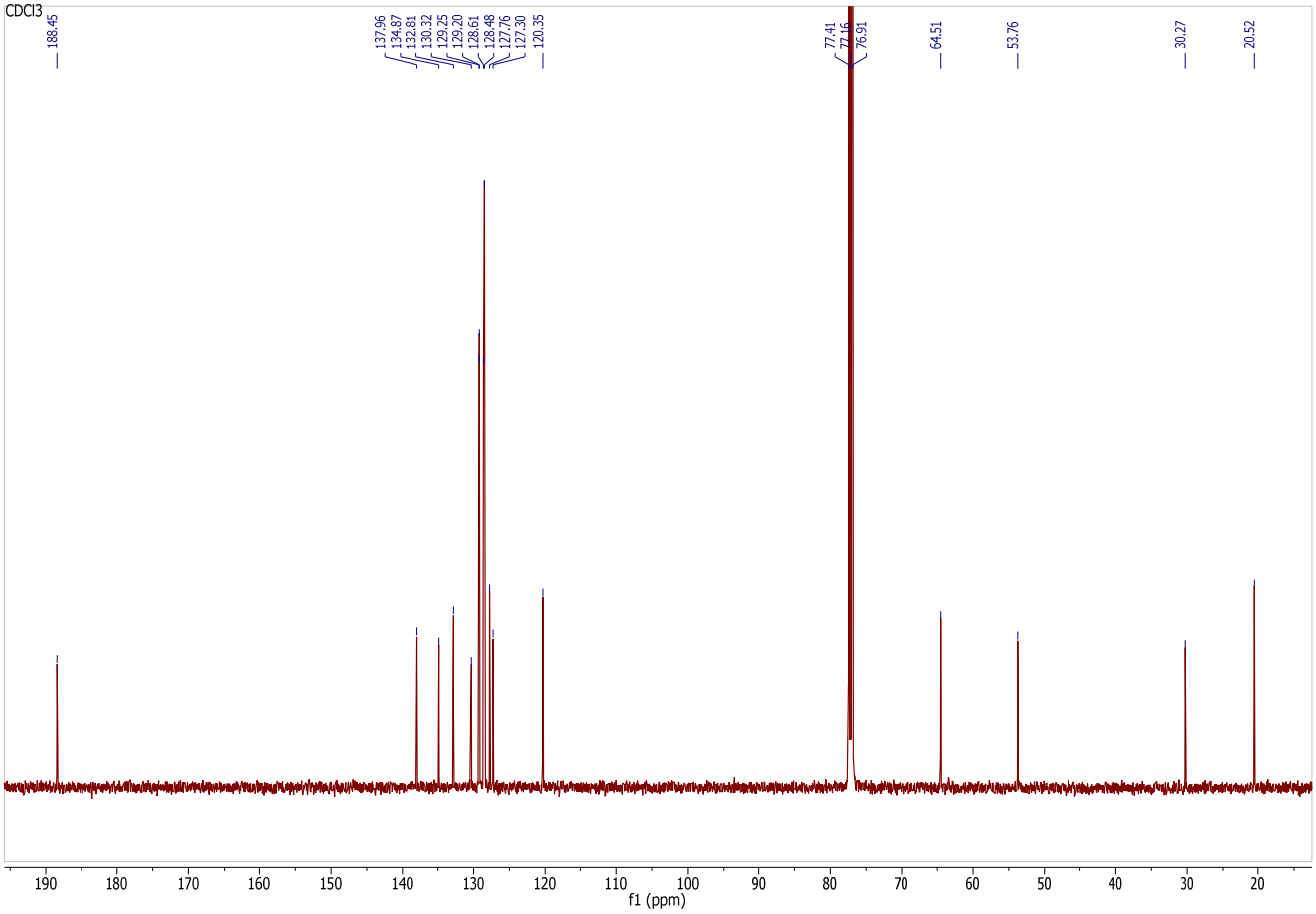

CDCl3
f2 (ppm)
f1 (ppm)


CDCl3
f2 (ppm)
f1 (ppm)



6b




CDCl3
188.45
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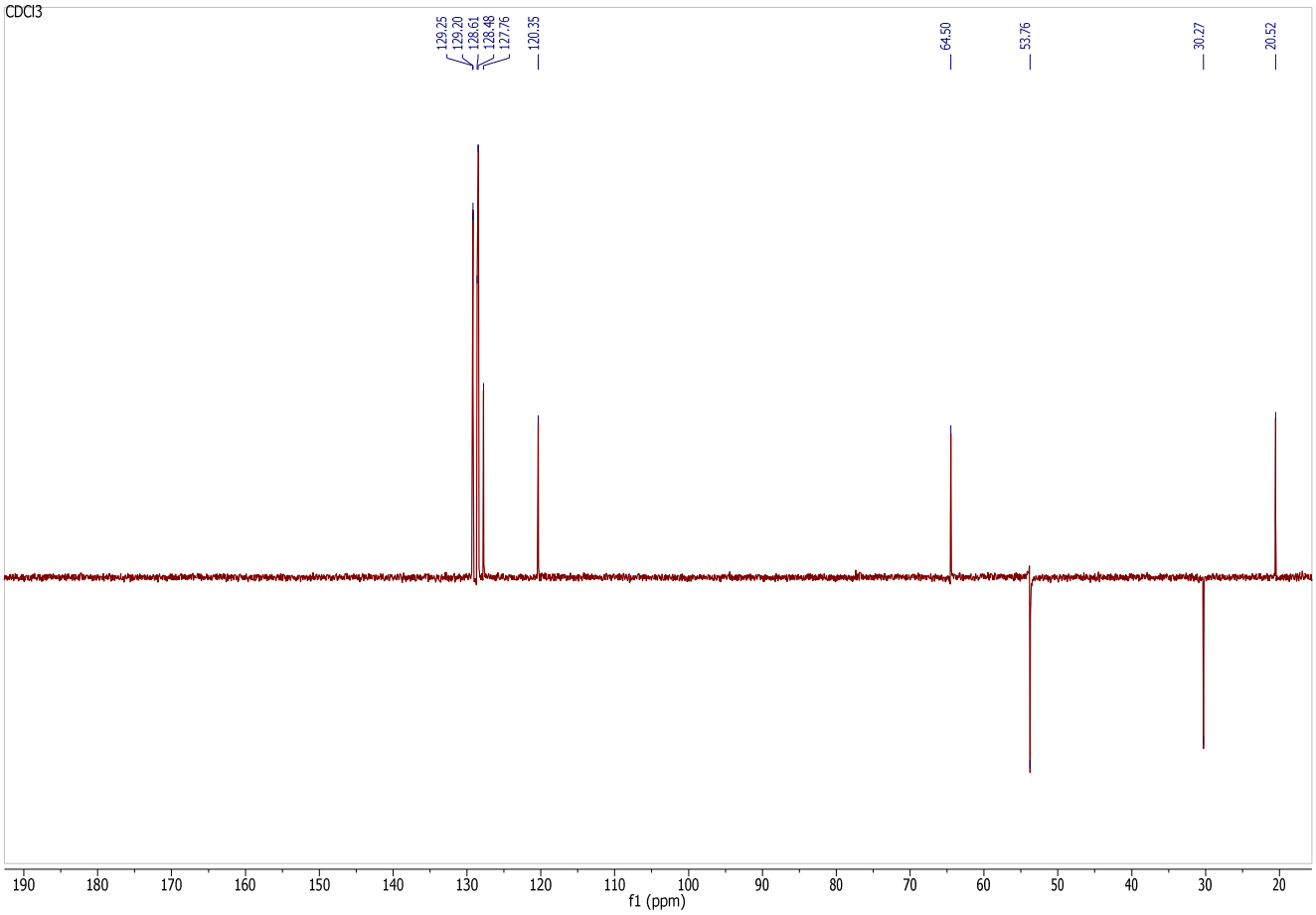
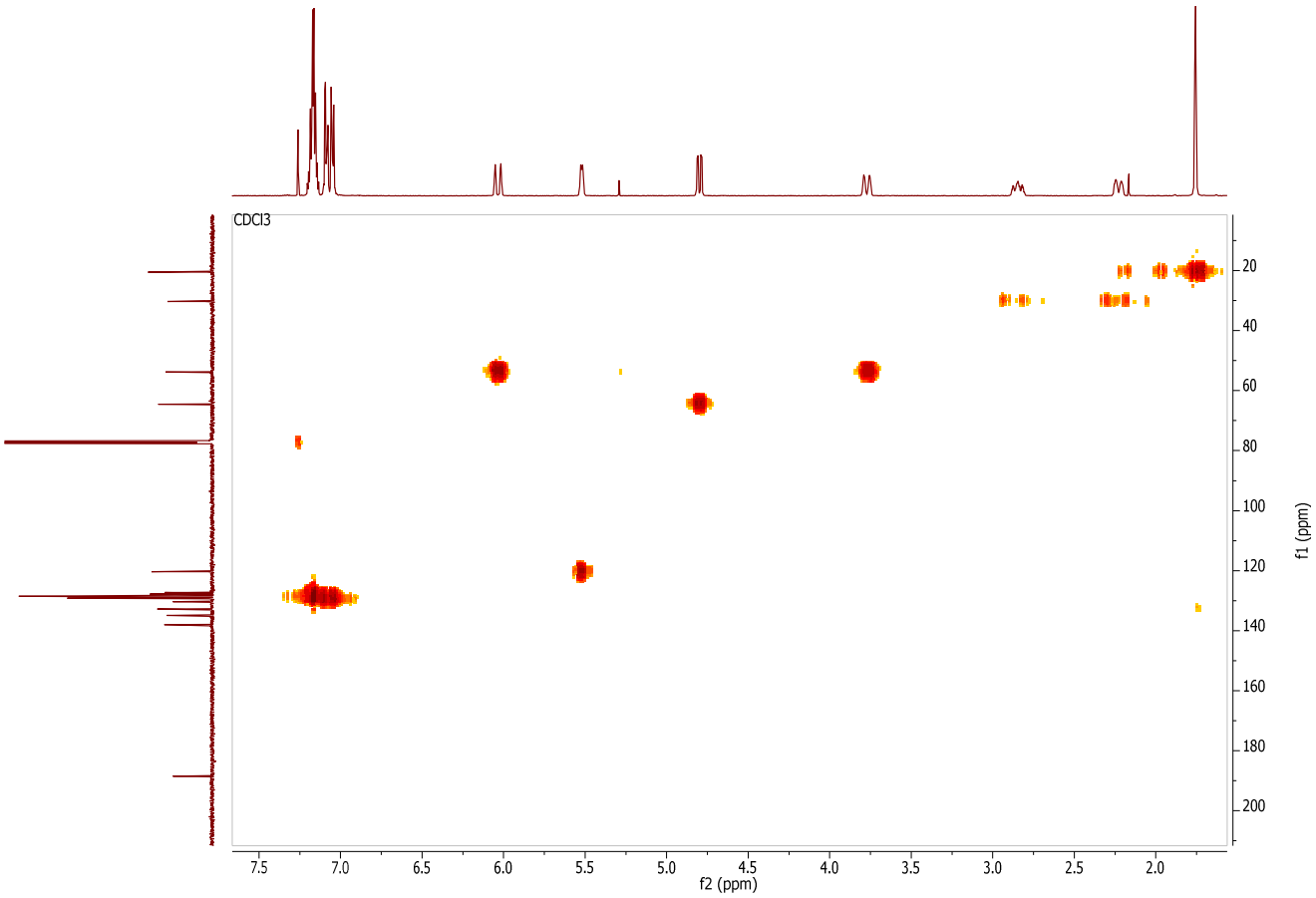
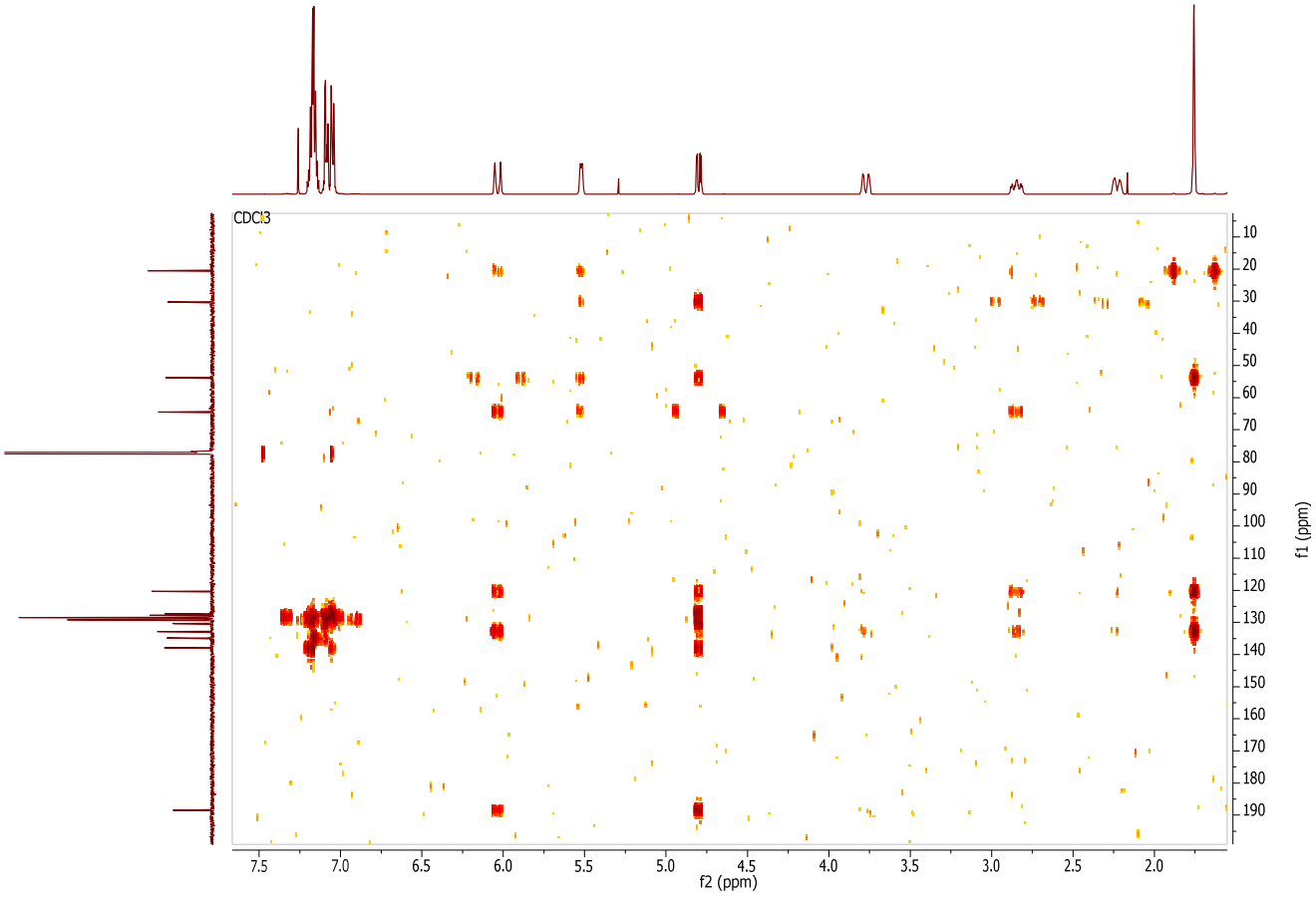
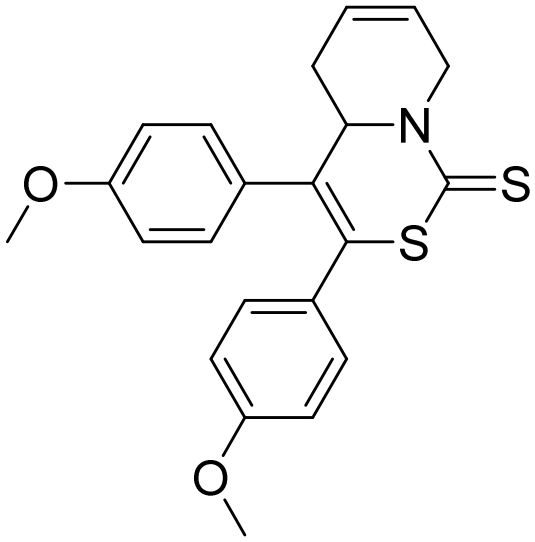
134.87
132.81
130.32
129.25
129.20
128.61
128.48
127.76
127.30
120.35
77.41
77.16
76.91
64.51
53.76
30.27
20.52
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
f1 (ppm)

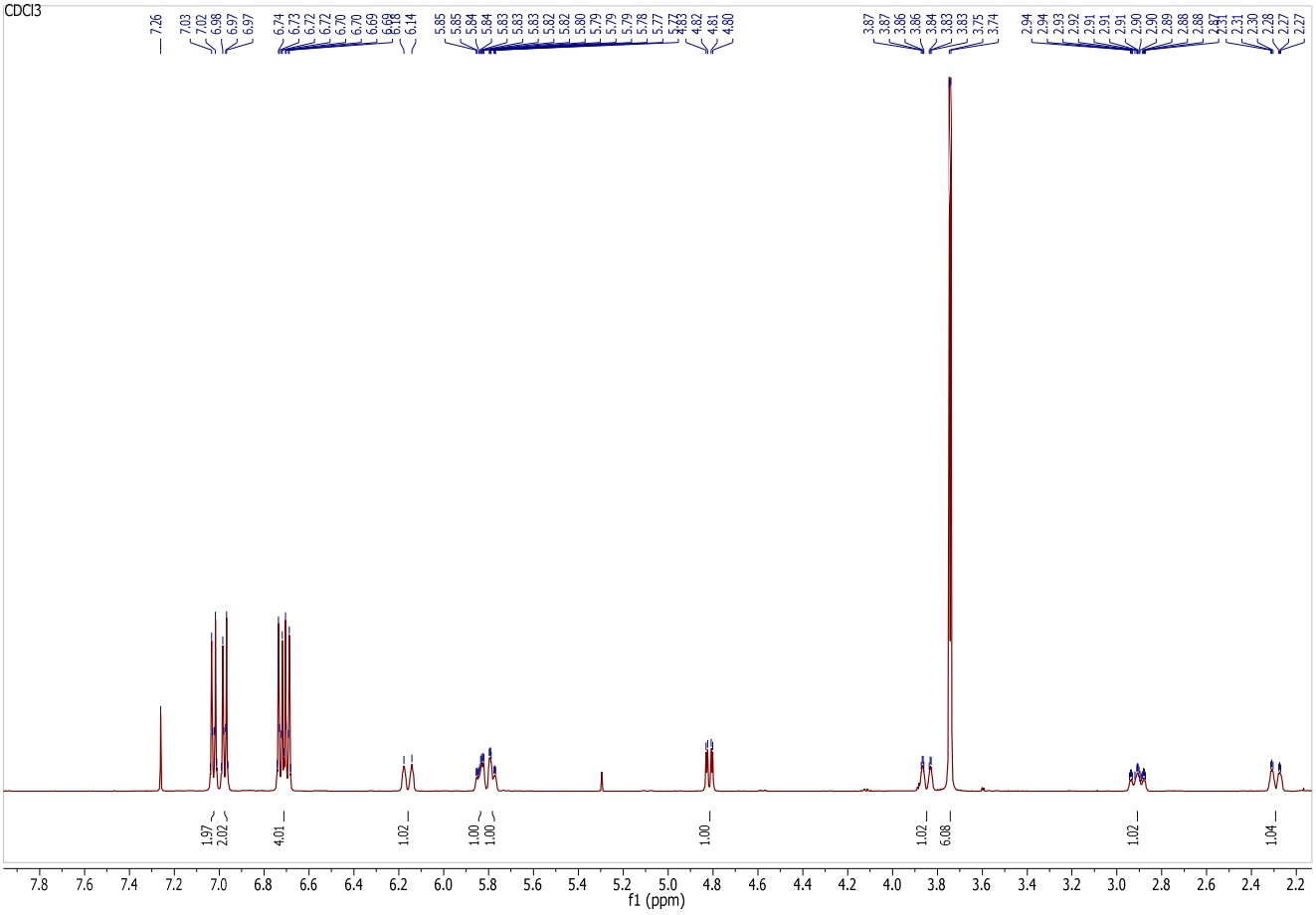

CDCl3
129.25
129.20
128.61
128.48
127.76
120.35
64.50
53.76
30.27
20.52
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
f1 (ppm)

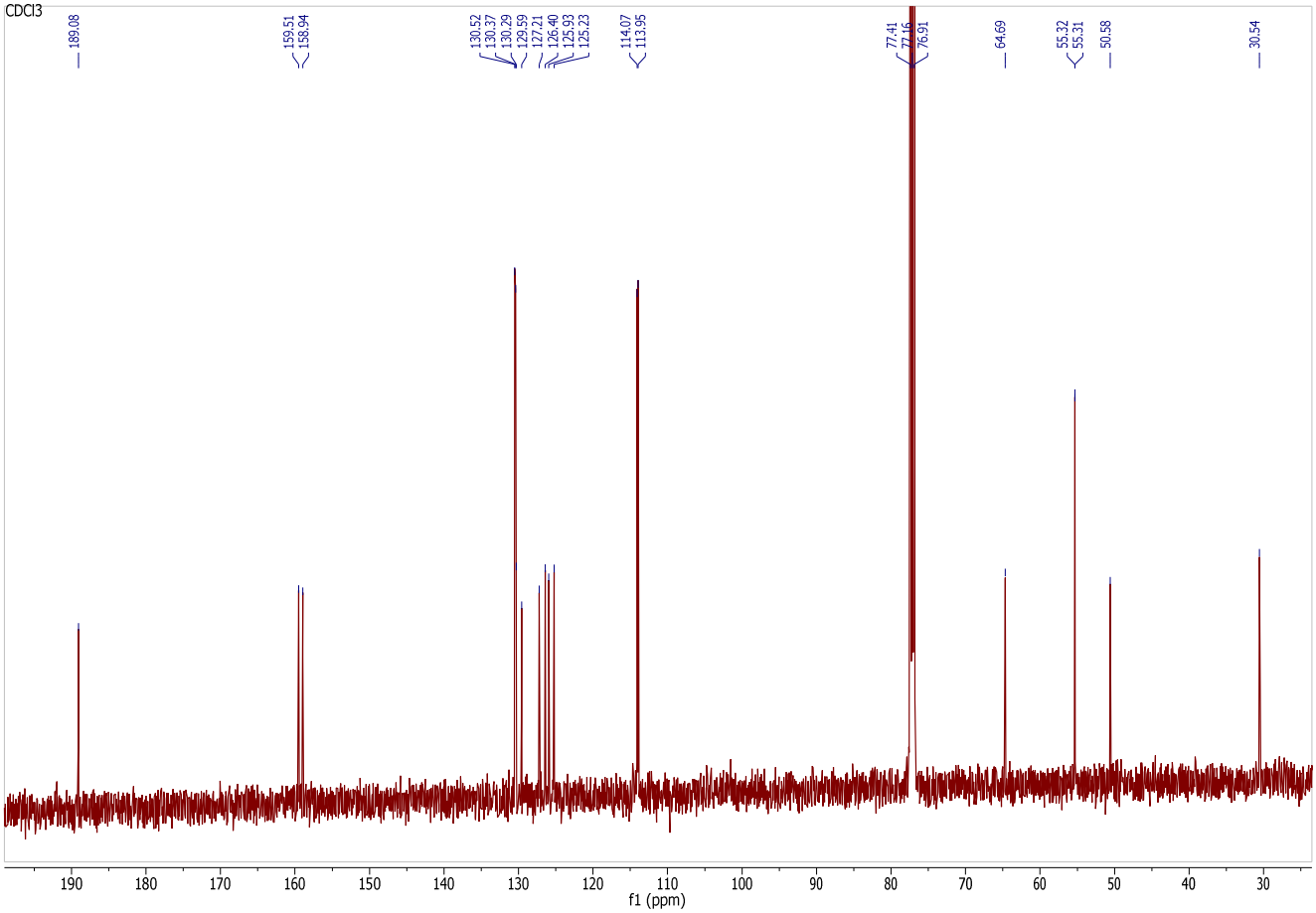

CDCl3
f1 (ppm)
f2 (ppm)

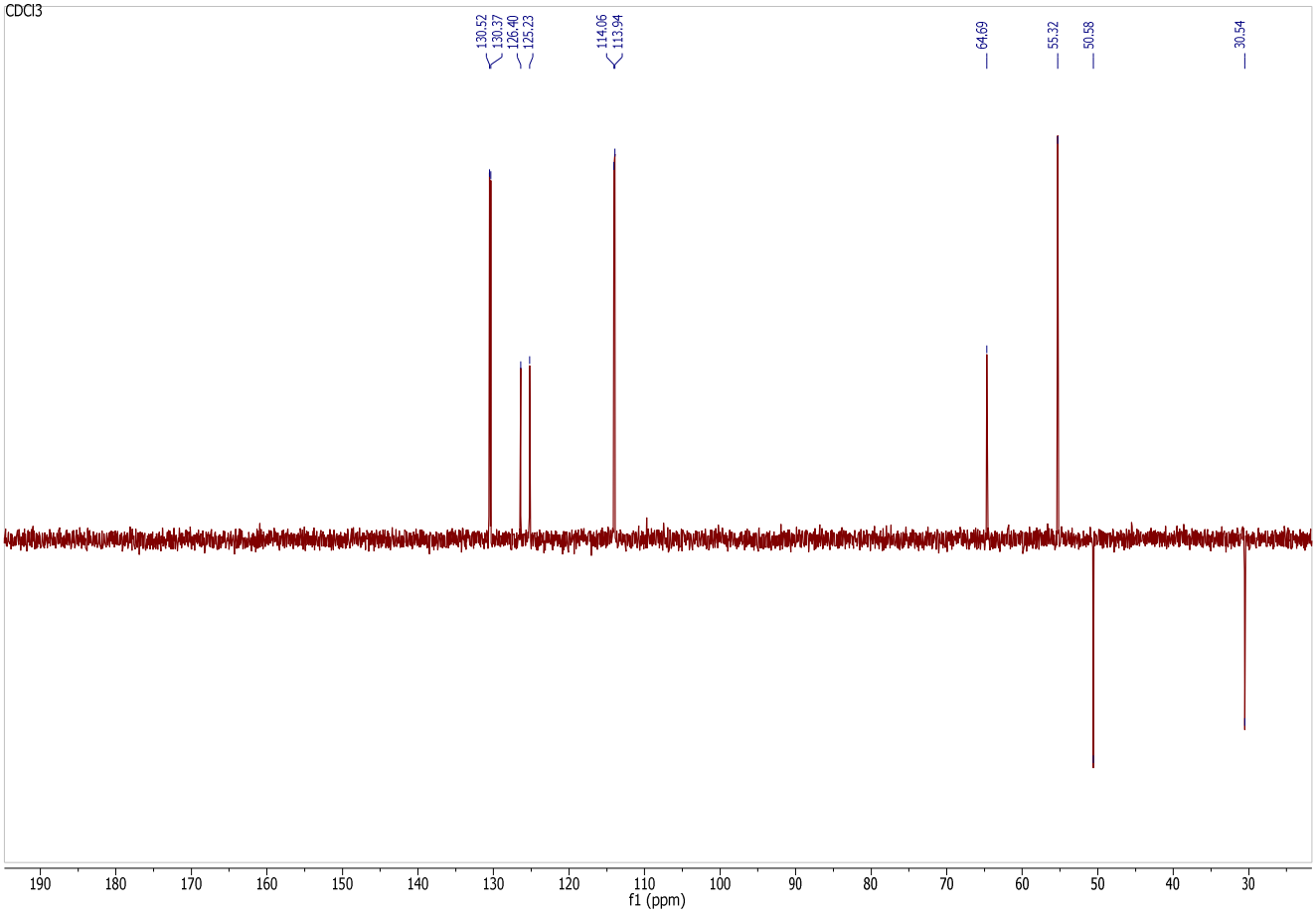

CDCl3
f1 (ppm)
f2 (ppm)

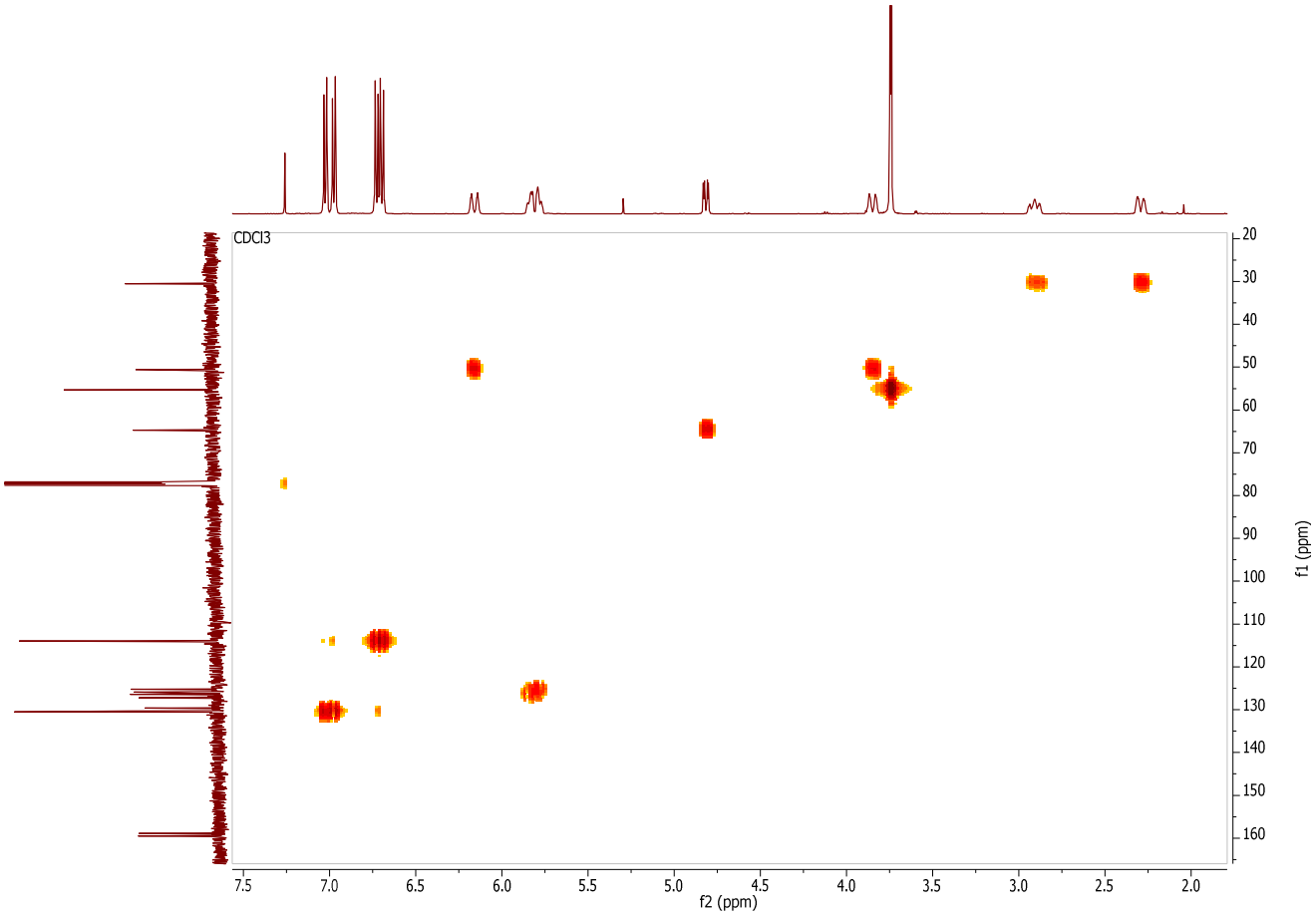


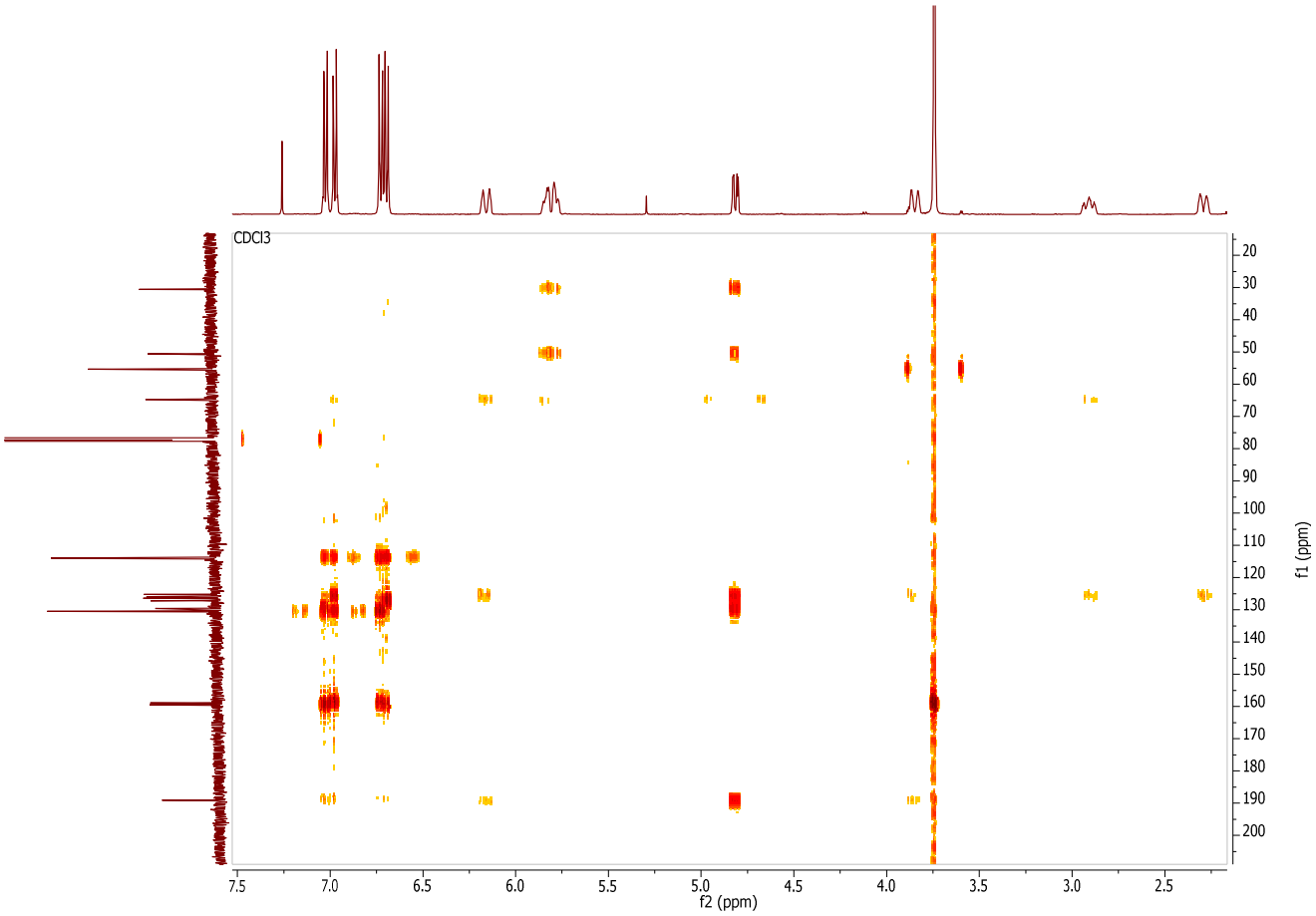
6c

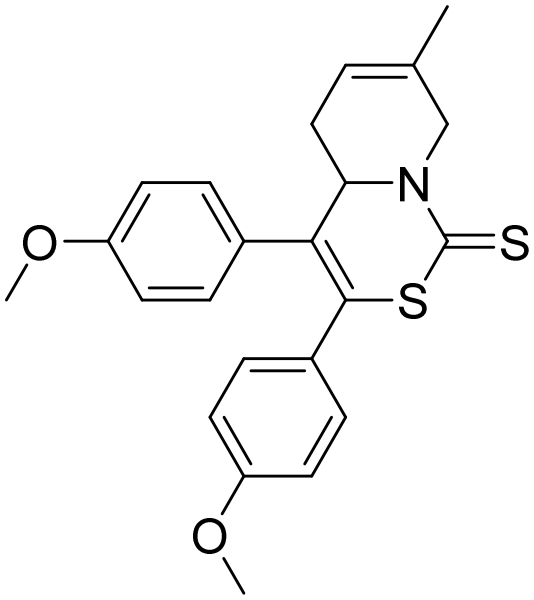



CDCl3
189.08
159.51
158.94
130.52
130.37
130.29
129.59
127.21
126.40
125.93
125.23
114.07
113.95
77.41
77.16
76.91
64.69
55.32
55.31
50.58
30.54
f1 (ppm)

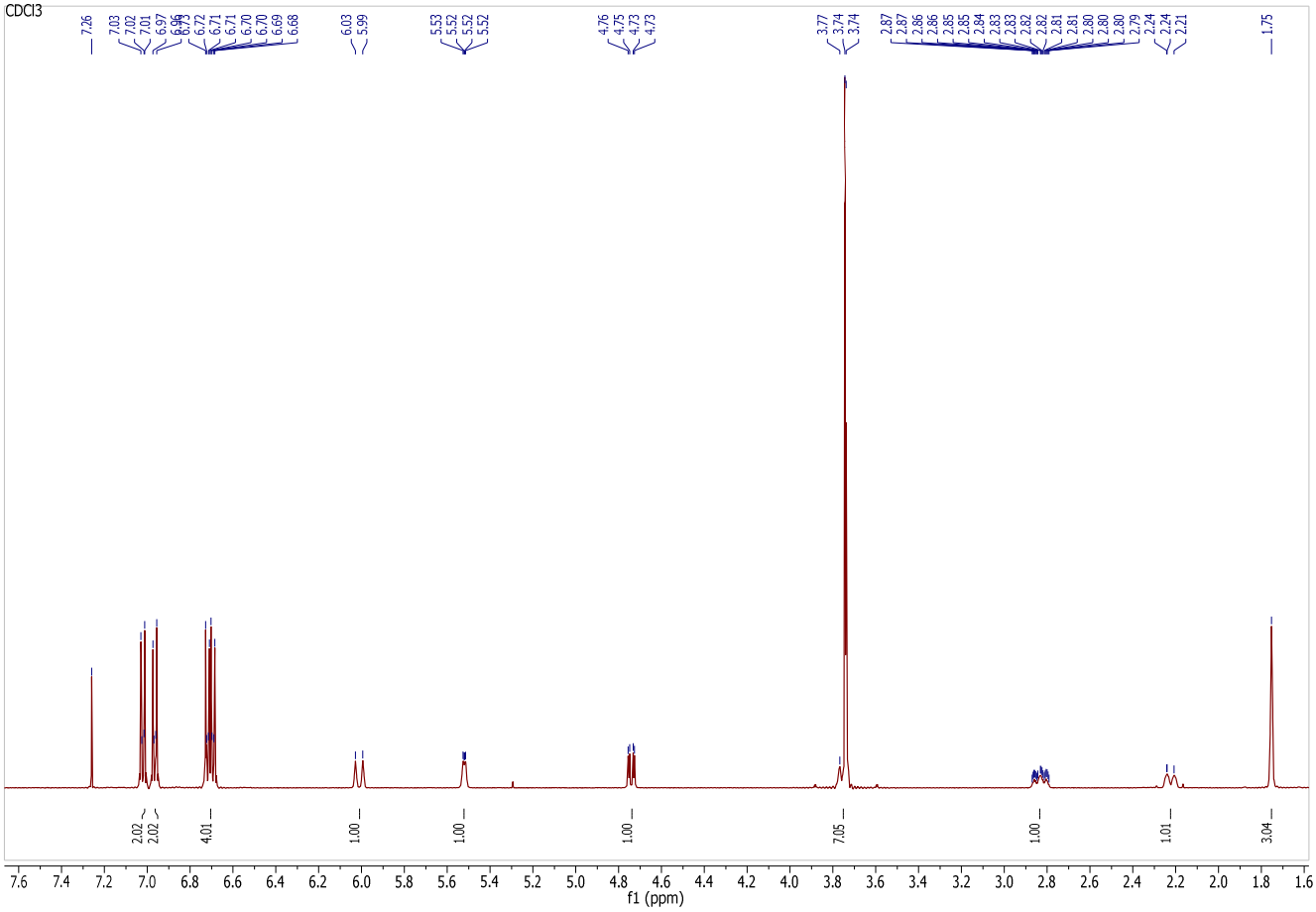

CDCl3
130.52
130.37
126.40
125.23
114.06
113.94
64.69
55.32
50.58
30.54
f1 (ppm)

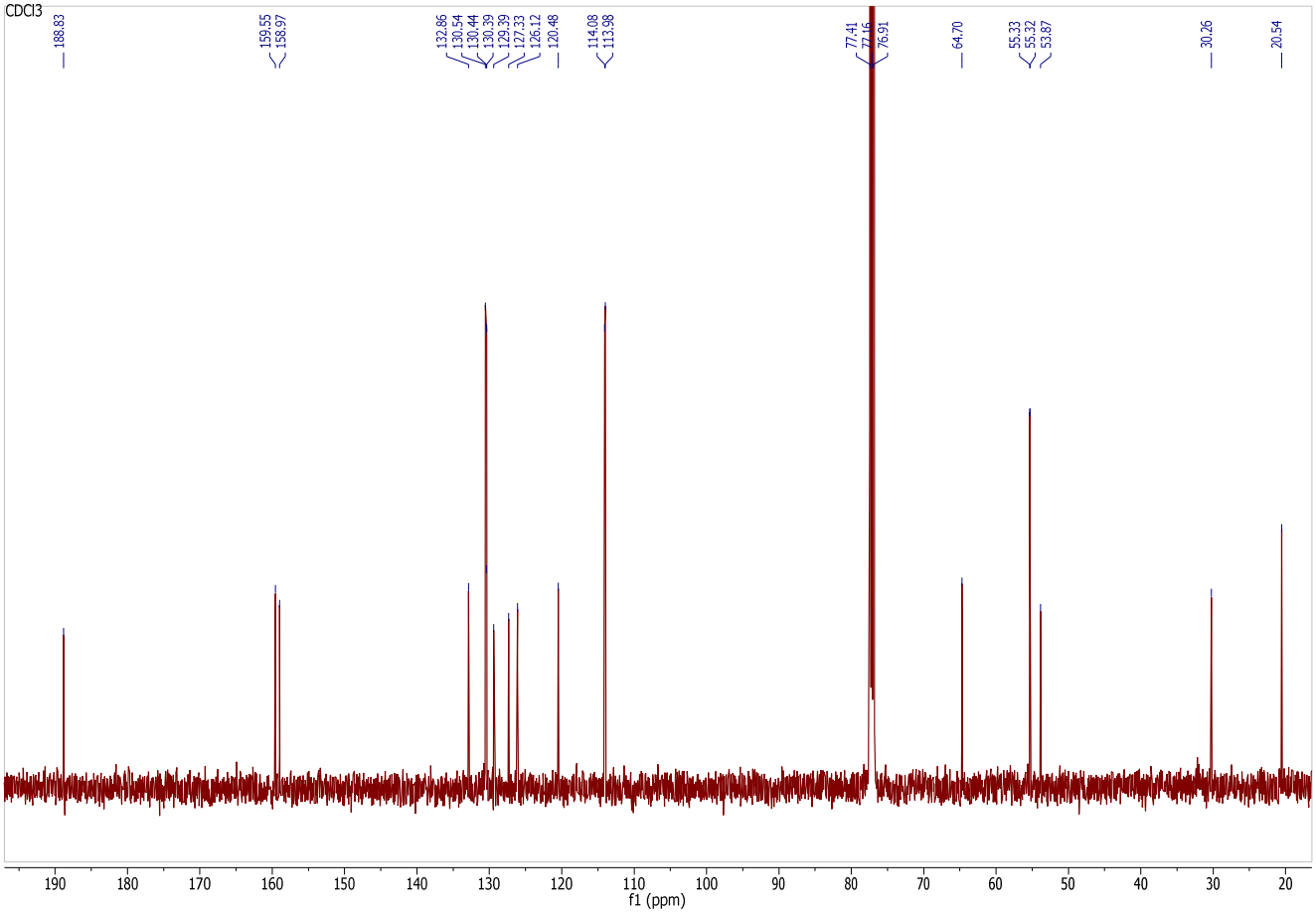

CDCl3
f2 (ppm)
f1 (ppm)


CDCl3
f2 (ppm)
f1 (ppm)



6d




CDCl3
188.83
159.55
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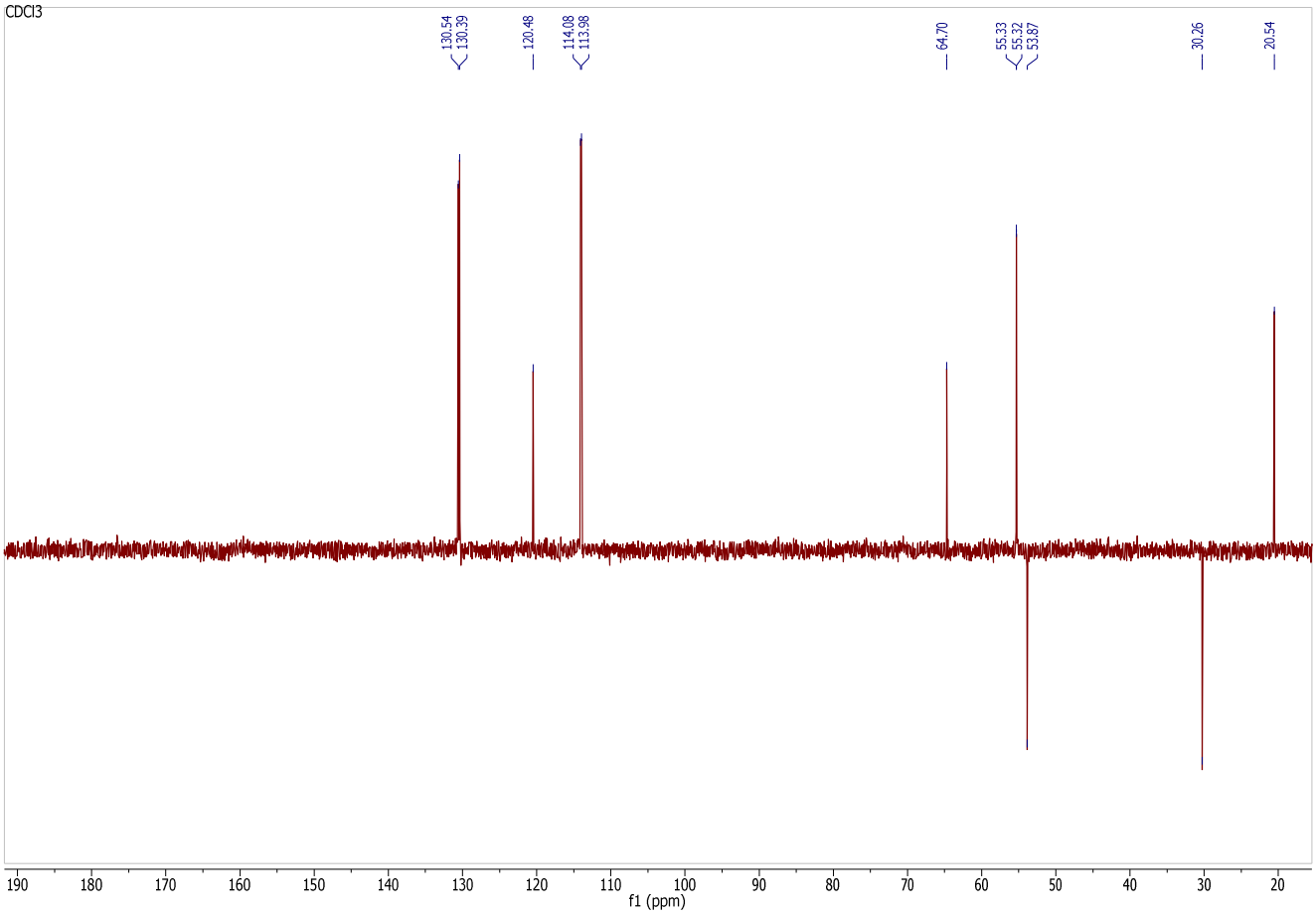
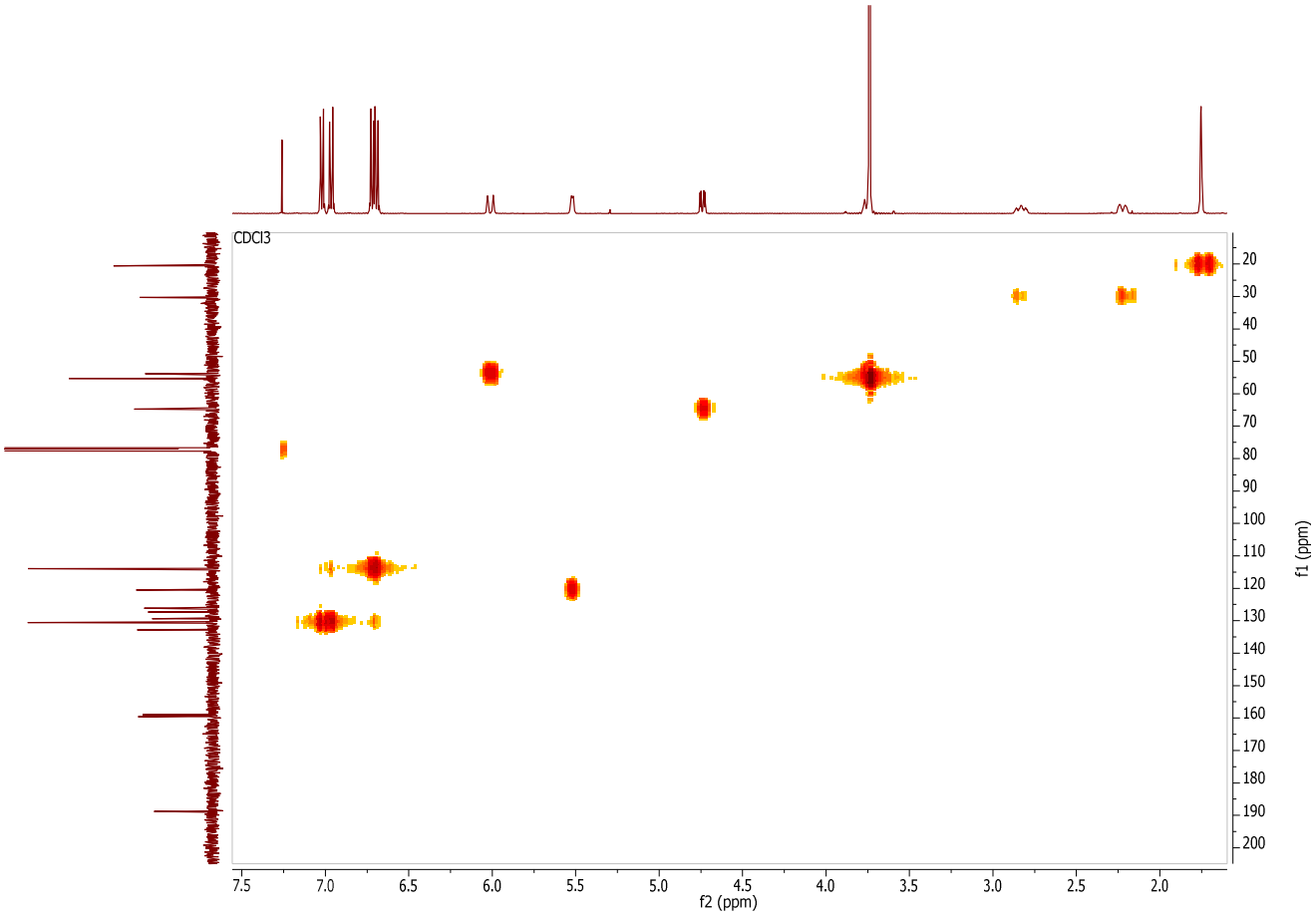
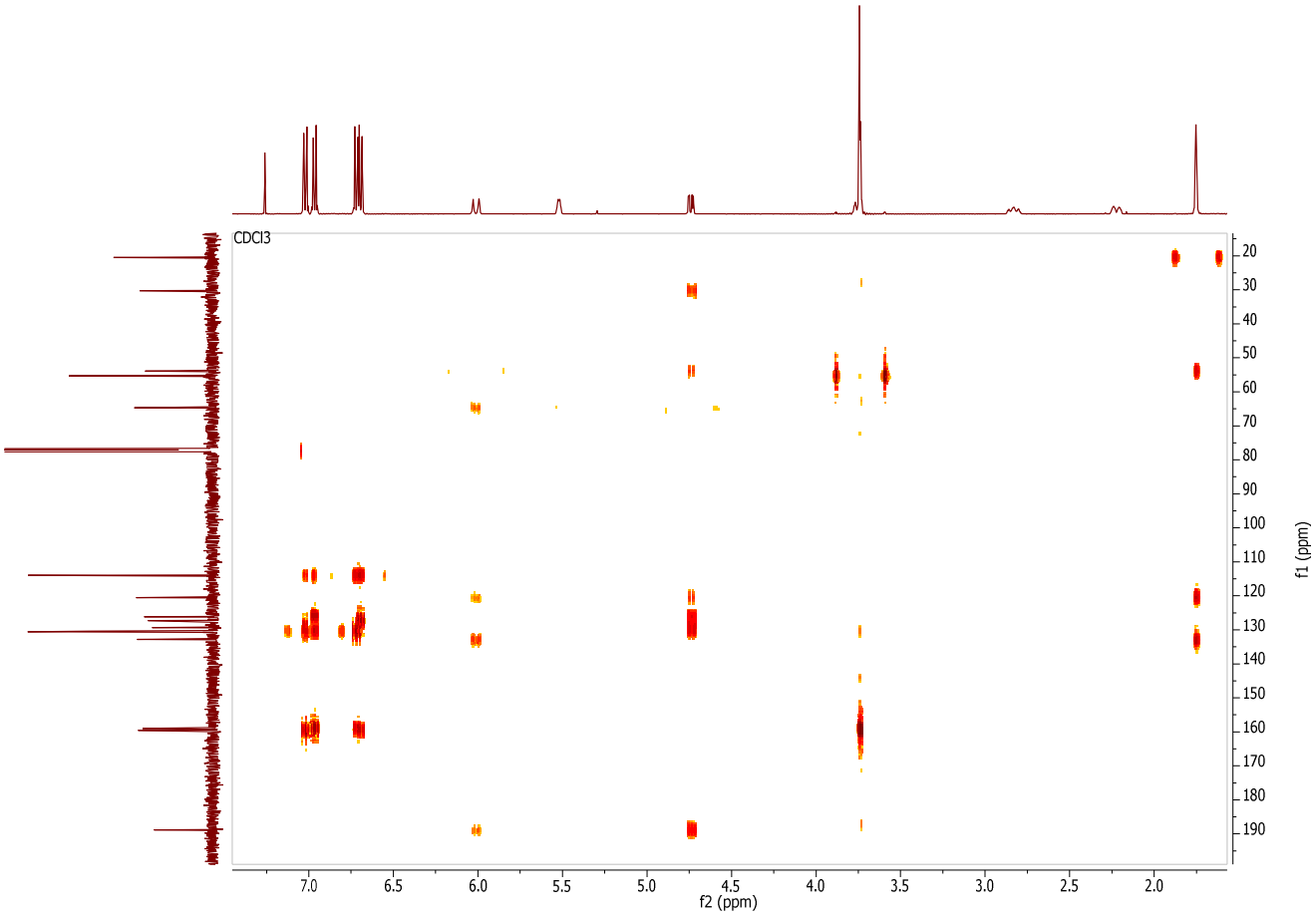
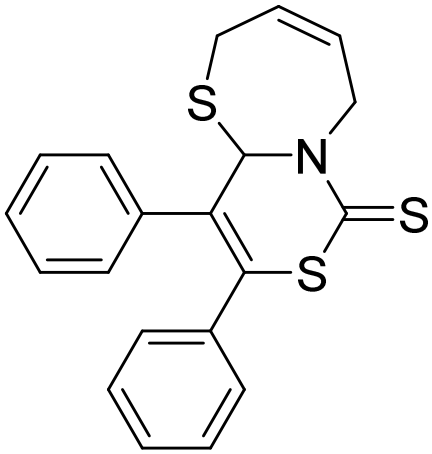
132.86
130.54
130.44
130.39
129.39
127.33
126.12
120.48
114.08
113.98
77.41
77.16
76.91
64.70
55.33
55.32
53.87
30.26
20.54
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
f1 (ppm)

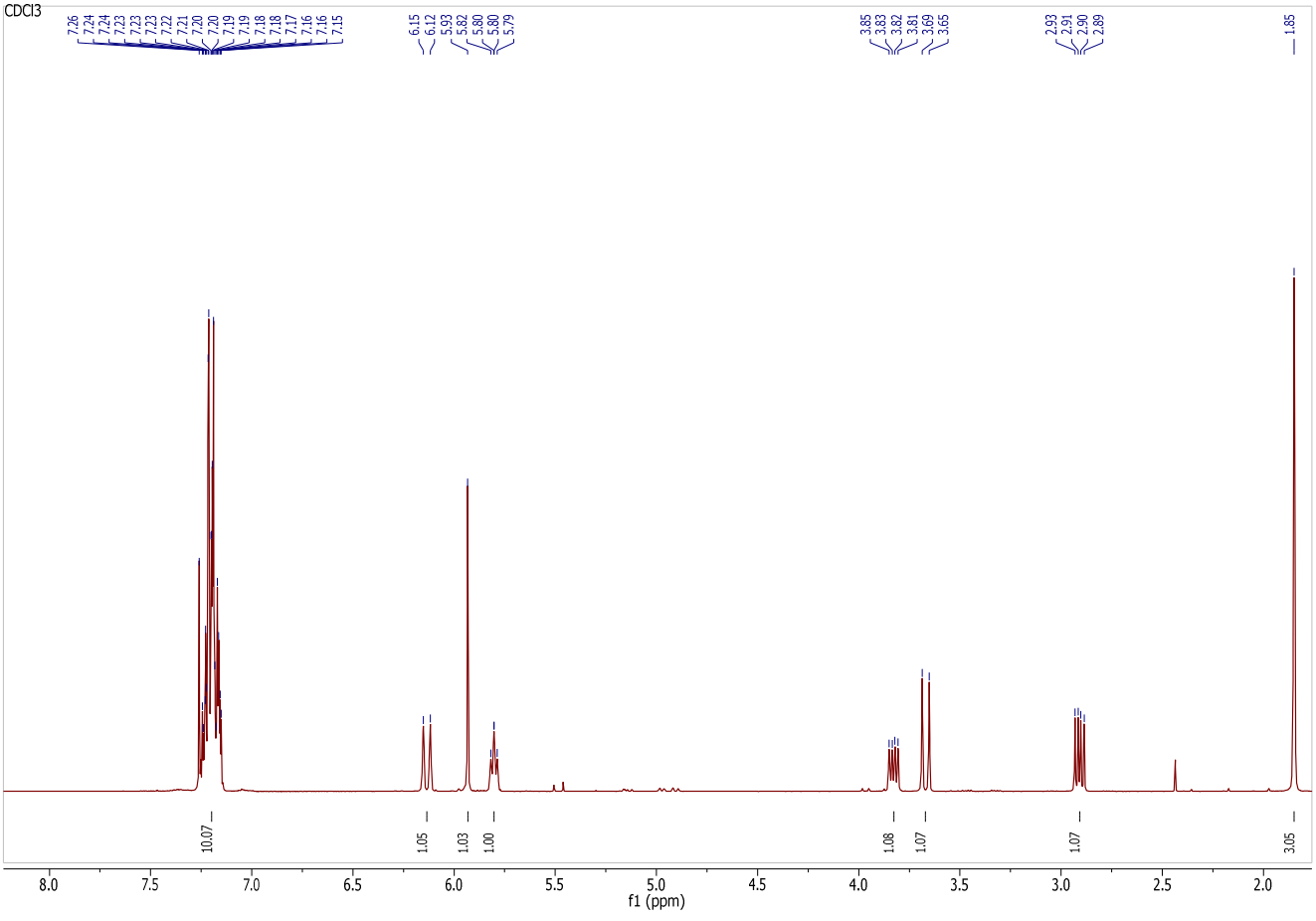

CDCl3
130.54
130.39
120.48
114.08
113.98
64.70
55.33
55.32
53.87
30.26
20.54
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
f1 (ppm)

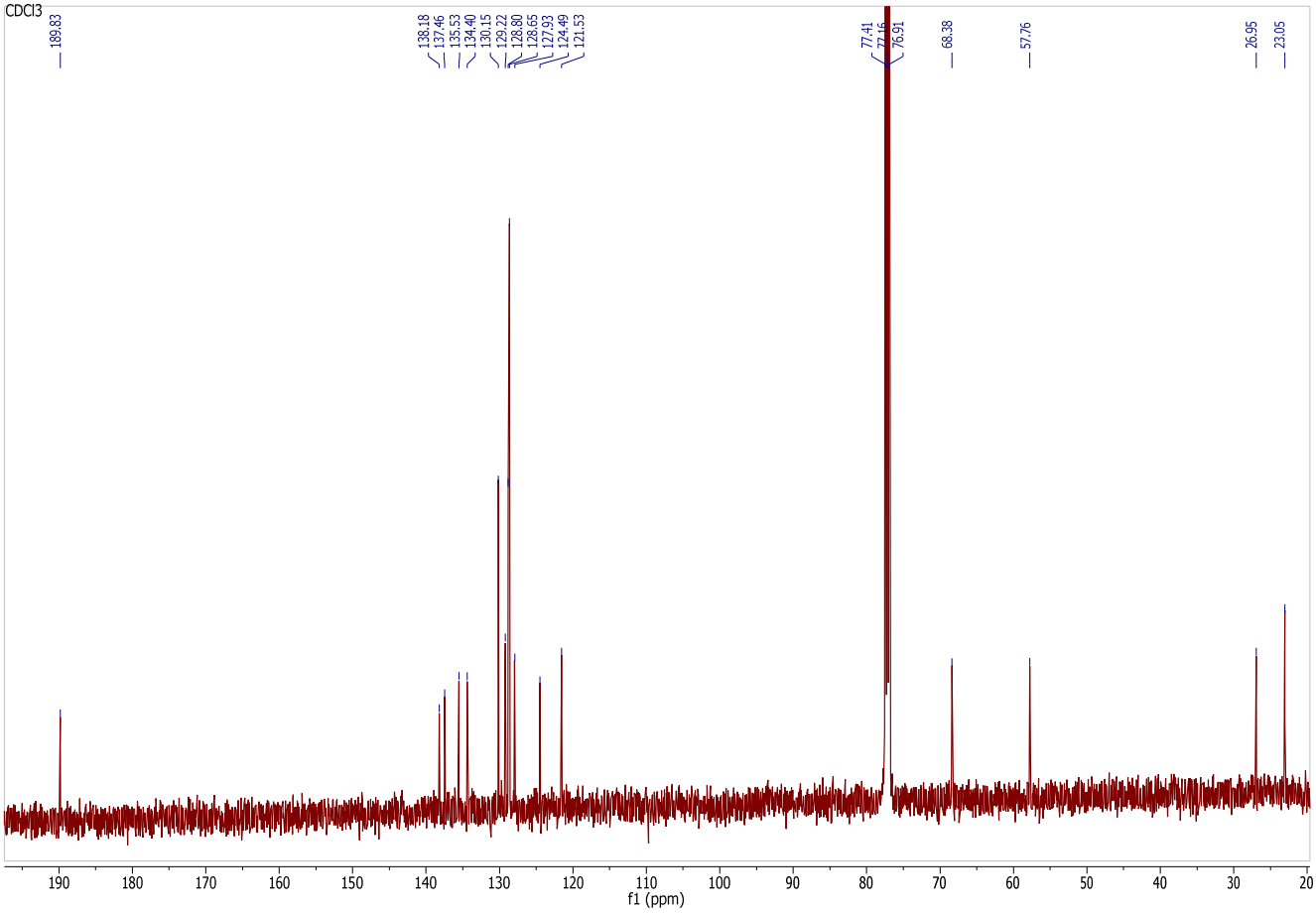

CDCl3
f2 (ppm)
f1 (ppm)

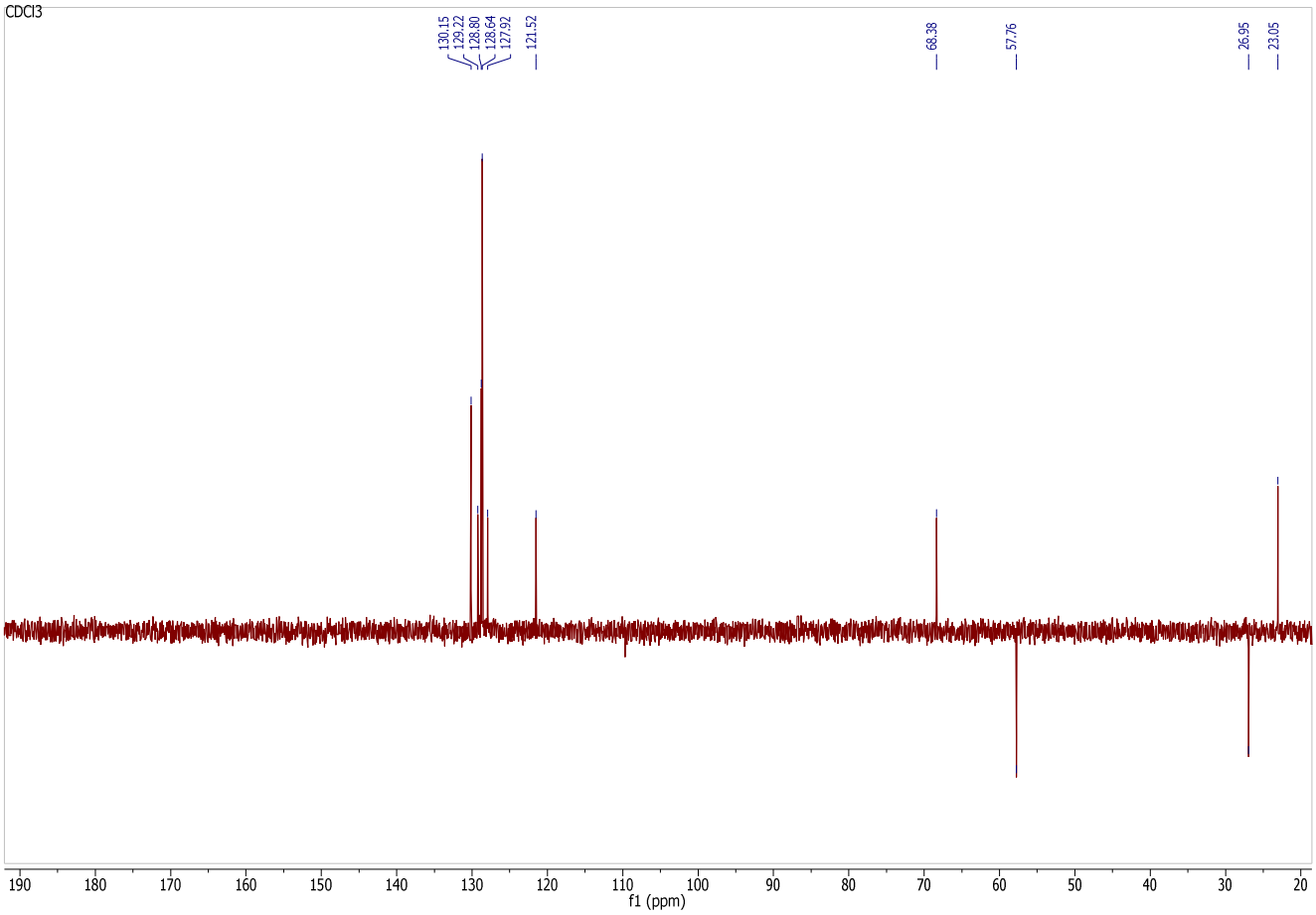

CDCl3
f2 (ppm)
f1 (ppm)

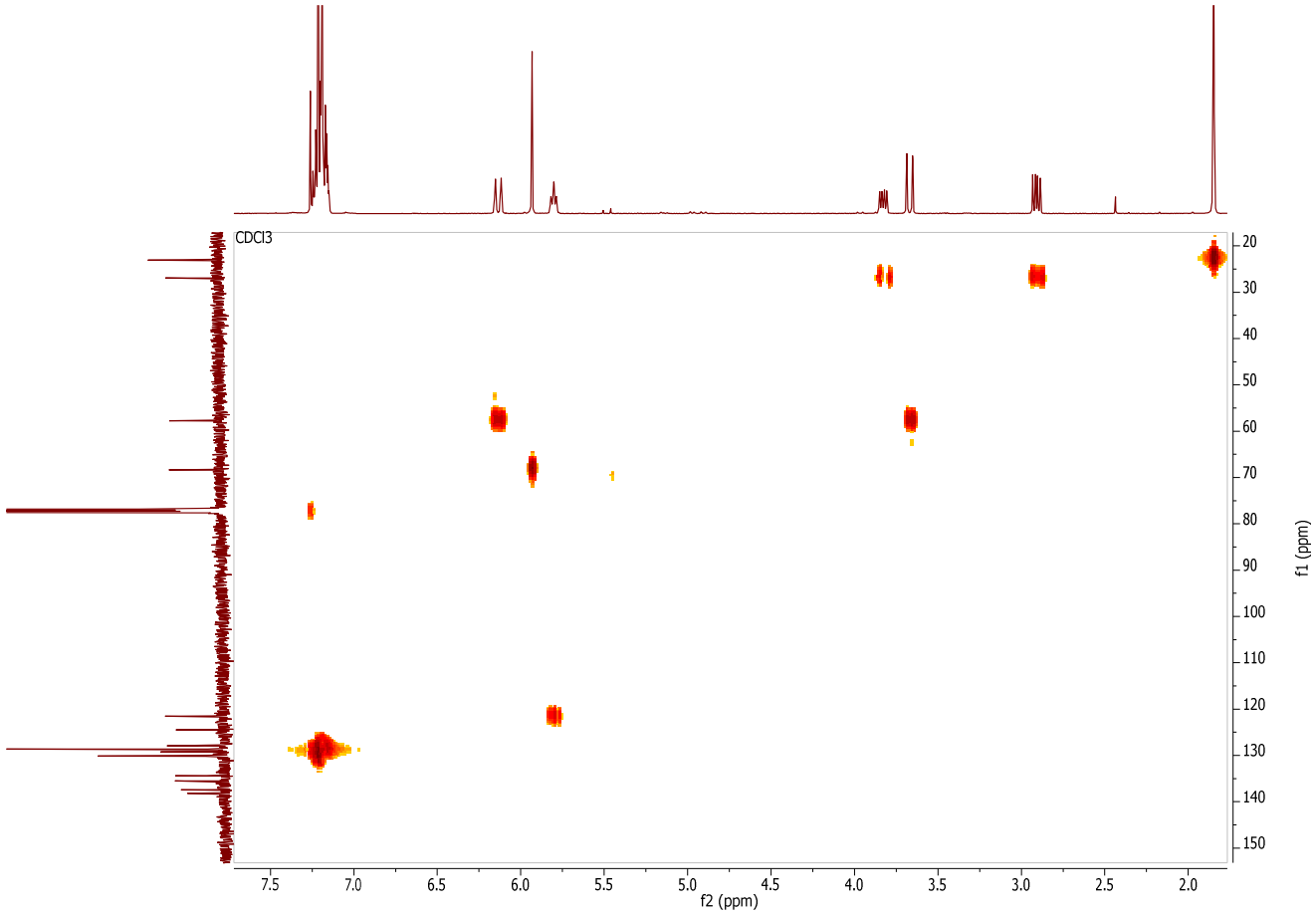

S
N
S
S

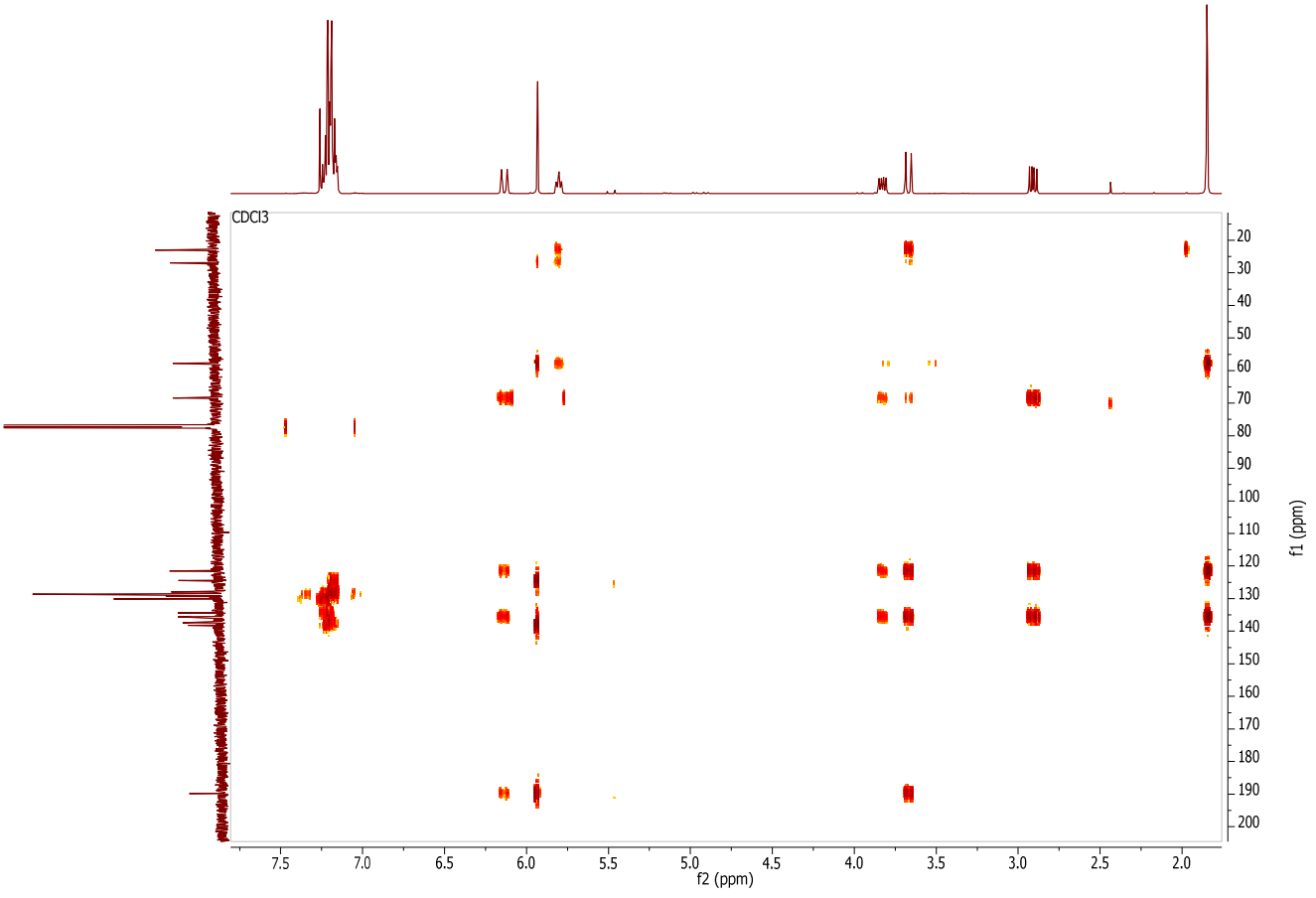
6e

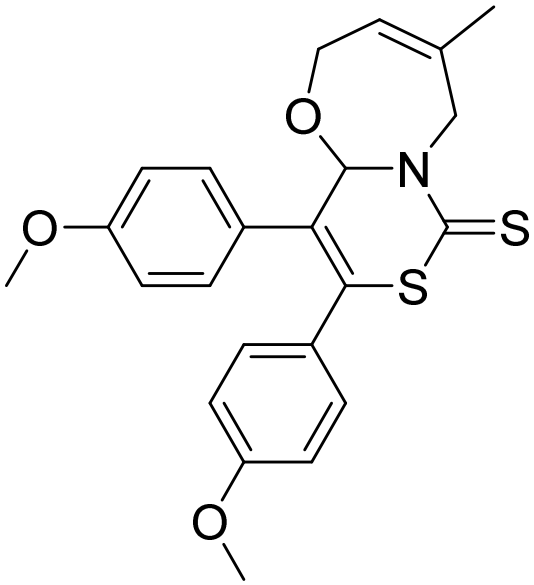

CDCl3
7.26
7.24
7.24
7.24
7.23
7.23
7.23
7.22
7.21
7.20
7.20
7.19
7.19
7.18
7.18
7.17
7.16
7.16
7.15
6.15
6.12
5.93
5.82
5.80
5.80
5.79
3.85
3.83
3.82
3.81
3.69
3.65
2.93
2.91
2.90
2.89
1.85
10.07
1.05
1.03
1.00
1.08
1.07
1.07
3.05
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
f1 (ppm)


CDCl3
189.83
138.18
137.46
135.53
134.40
130.15
129.22
128.80
128.65
127.93
124.49
121.53
77.41
77.16
76.91
68.38
57.76
26.95
23.05
f1 (ppm)

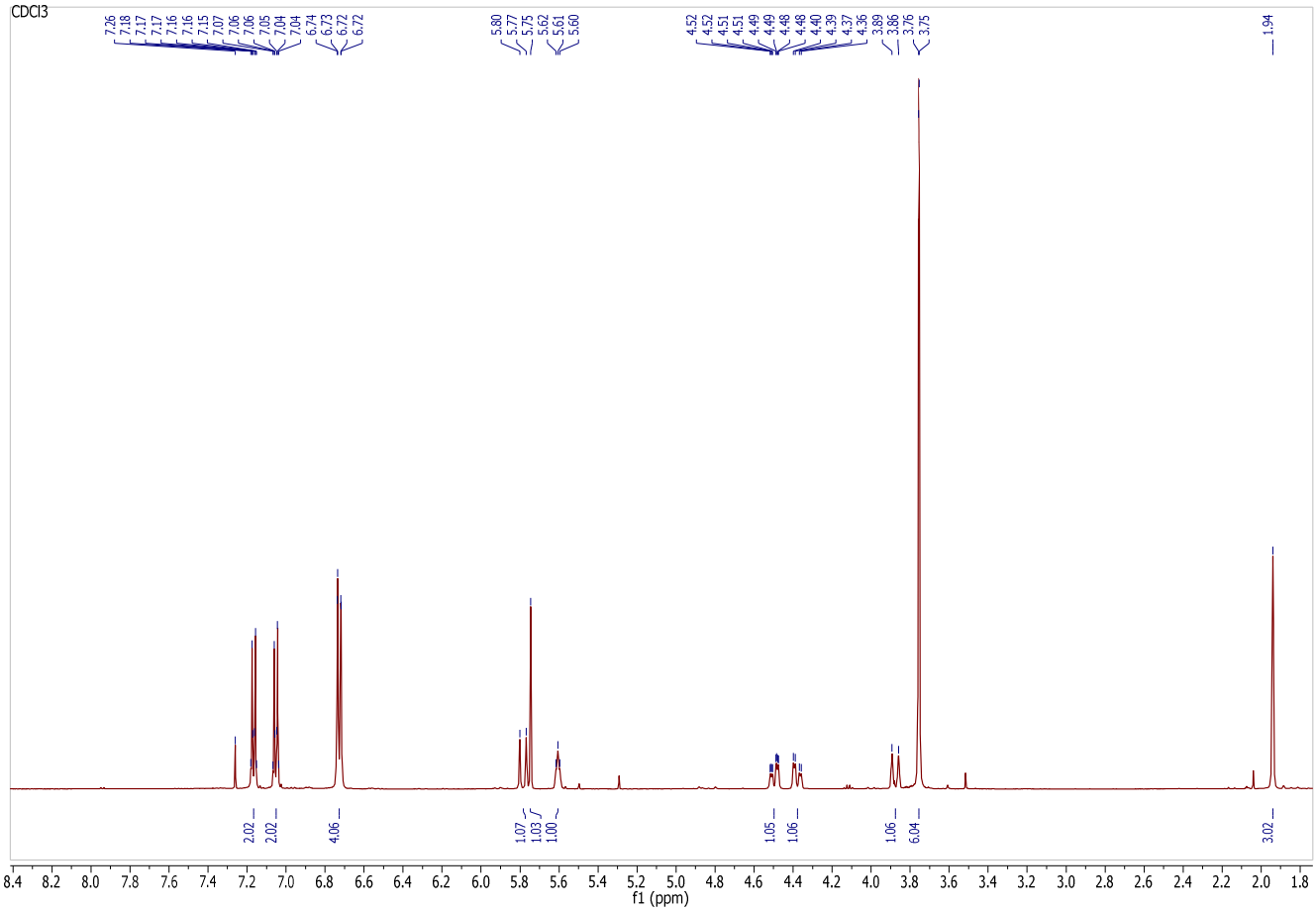

CDCl3
130.15
129.22
128.80
128.64
127.92
121.52
68.38
57.76
26.95
23.05
f1 (ppm)

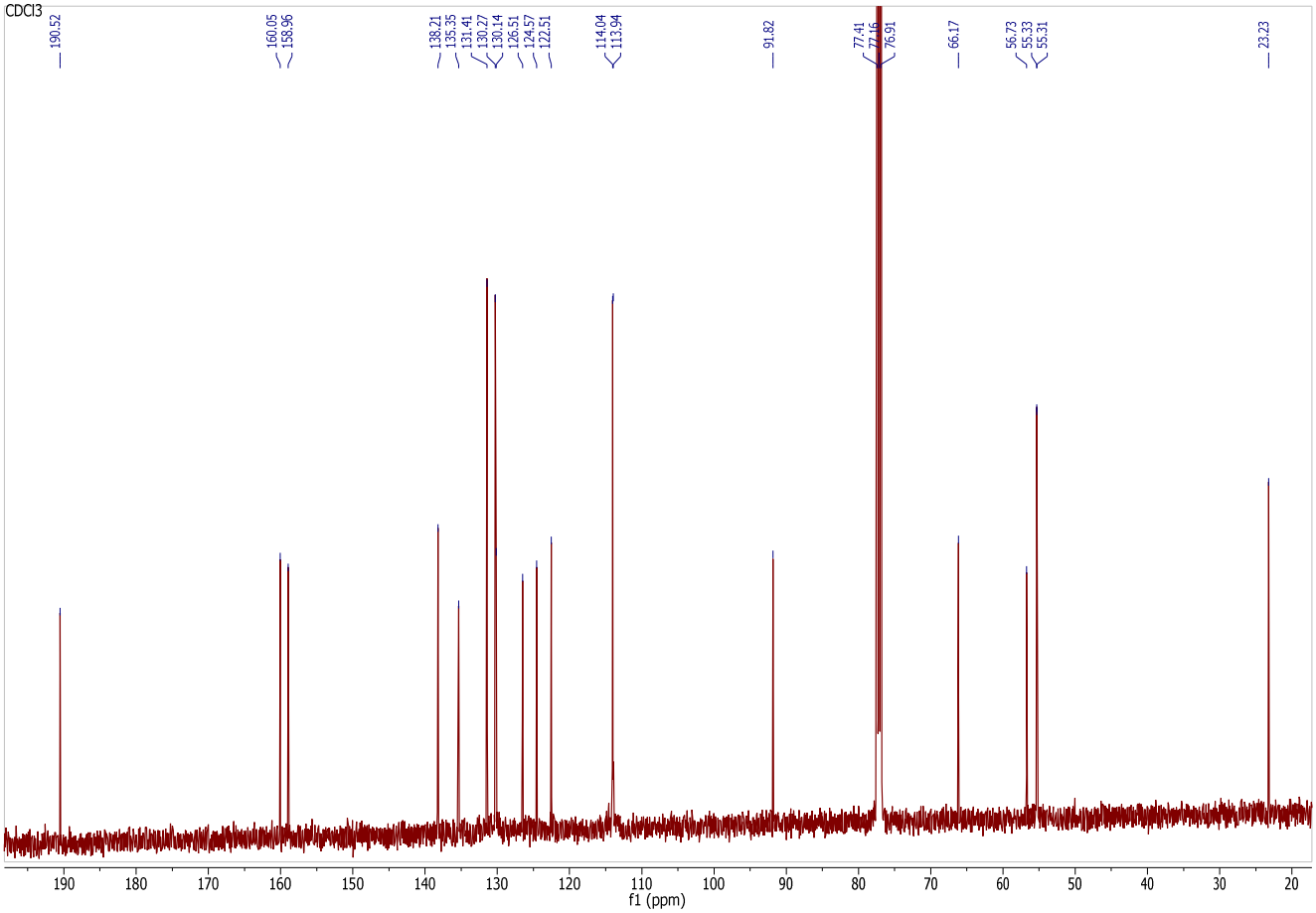

CDCl3
f2 (ppm)
f1 (ppm)

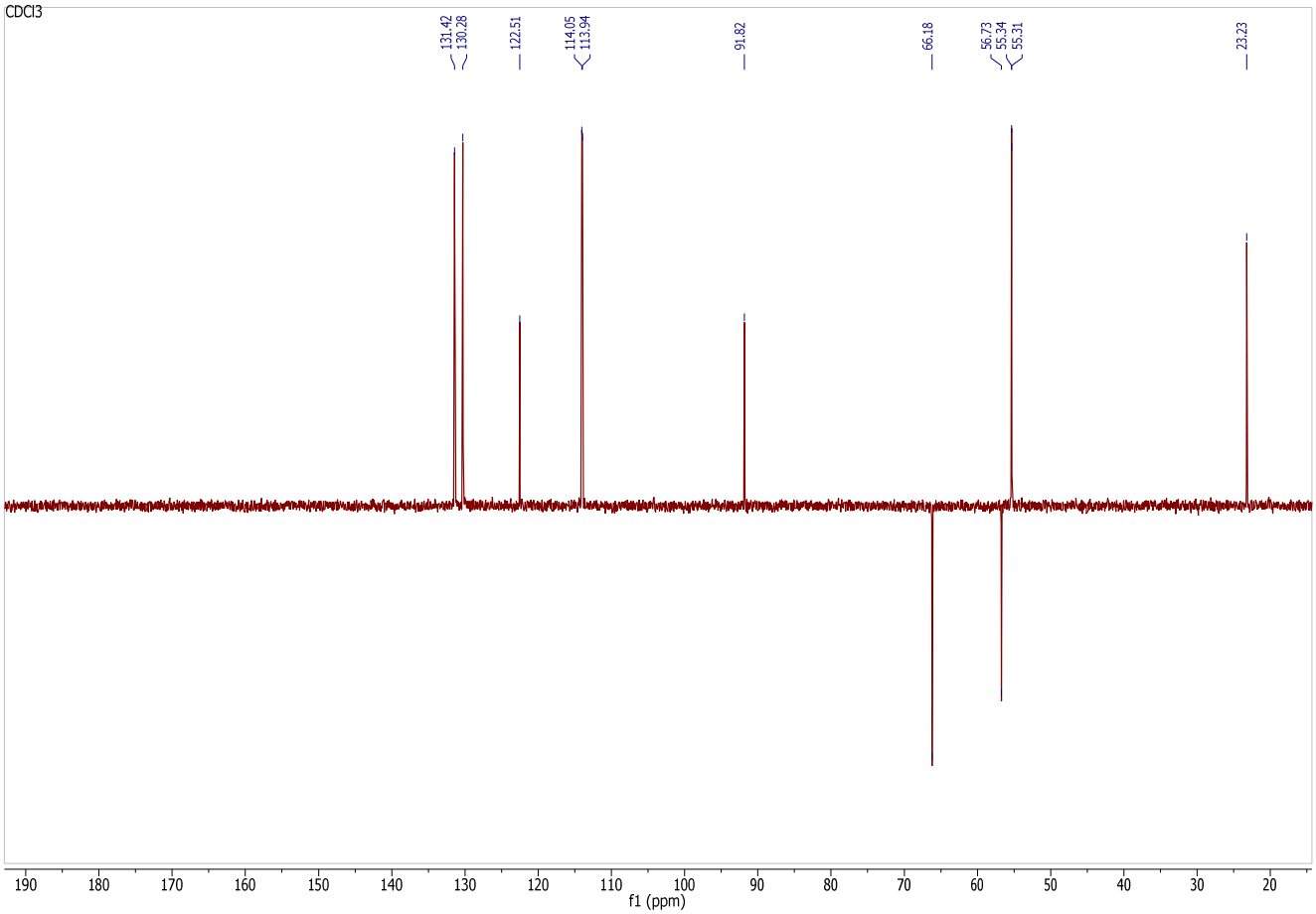

CDCl3
f2 (ppm)
f1 (ppm)

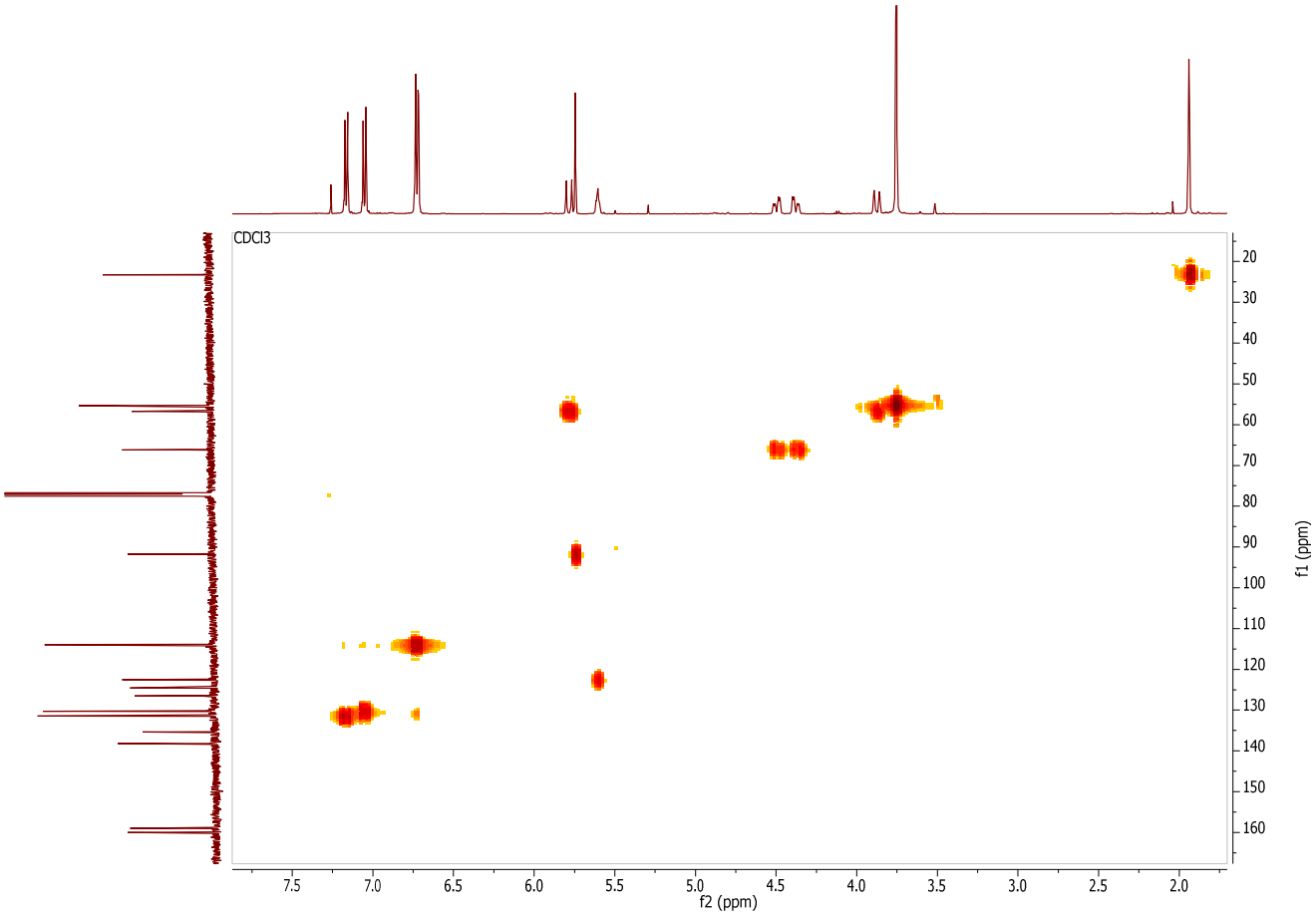


6f




CDCl3
190.52
160.05
158.96
138.21
135.35
131.41
130.27
130.14
126.51
124.57
122.51
114.04
113.94
91.82
77.41
77.16
76.91
66.17
56.73
55.33
55.31
23.23
f1 (ppm)


CDCl3
131.42
130.28
122.51
114.05
113.94
91.82
66.18
56.73
55.34
55.31
23.23
f1 (ppm)


CDCl3
f2 (ppm)
f1 (ppm)

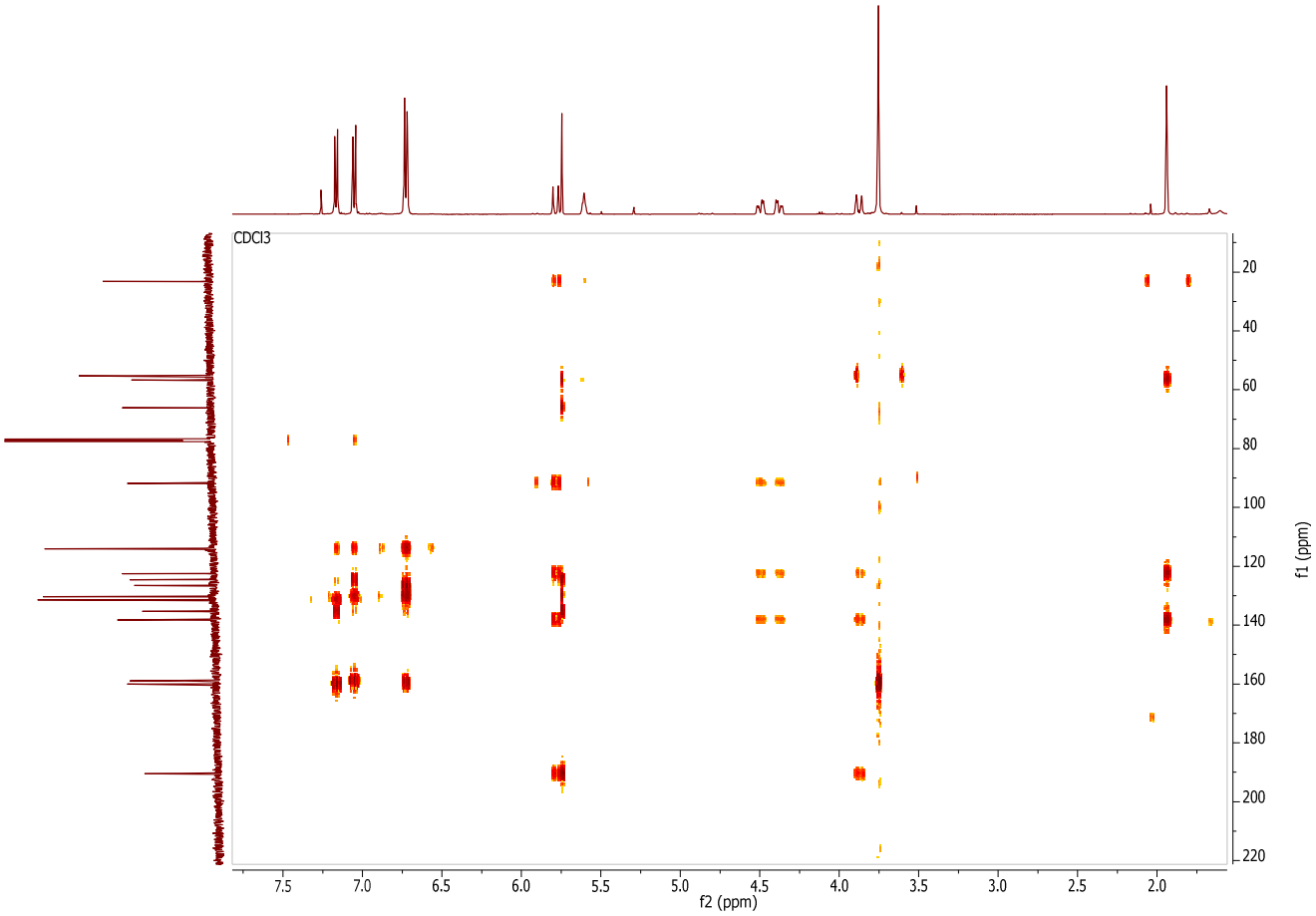
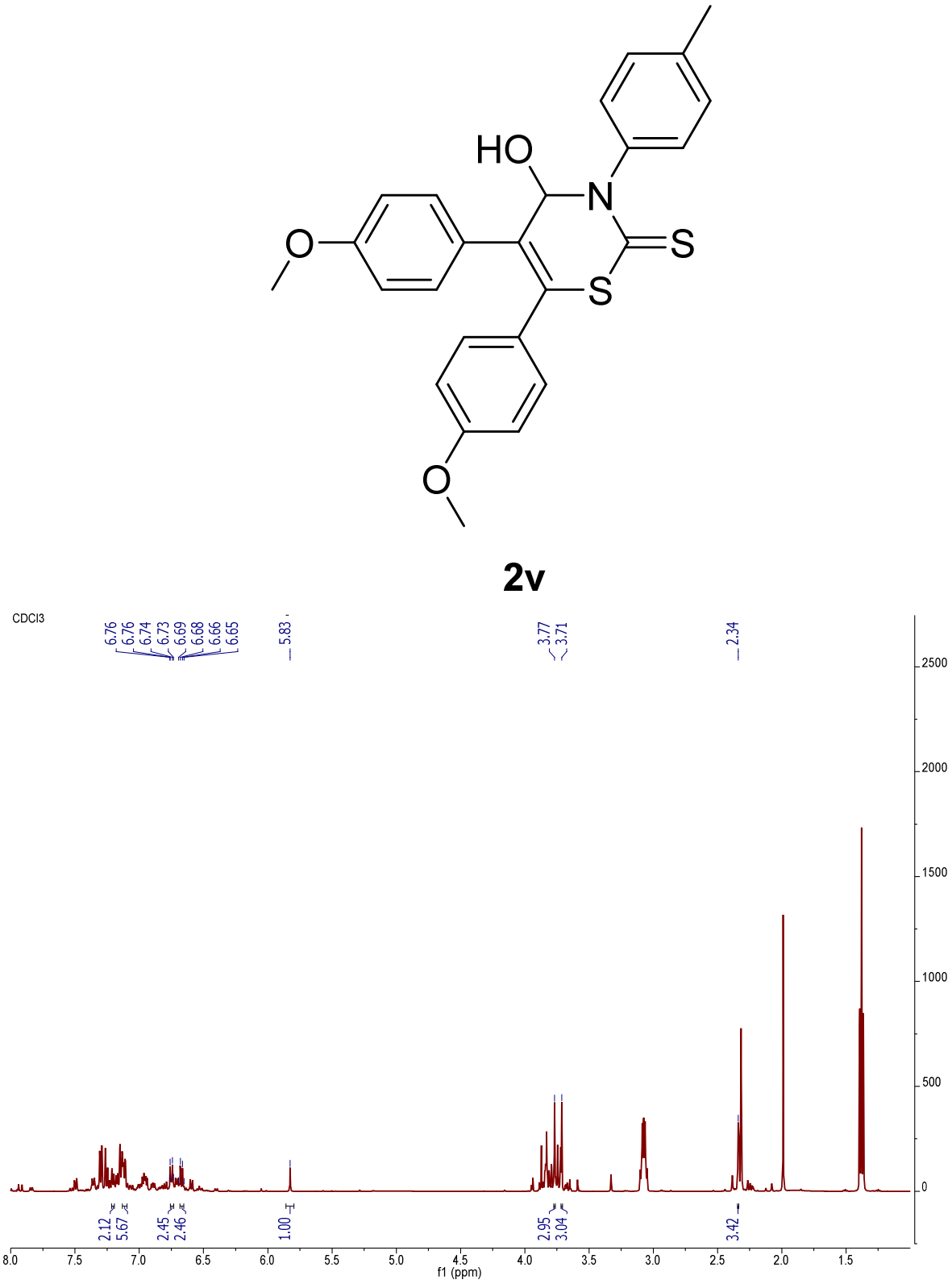
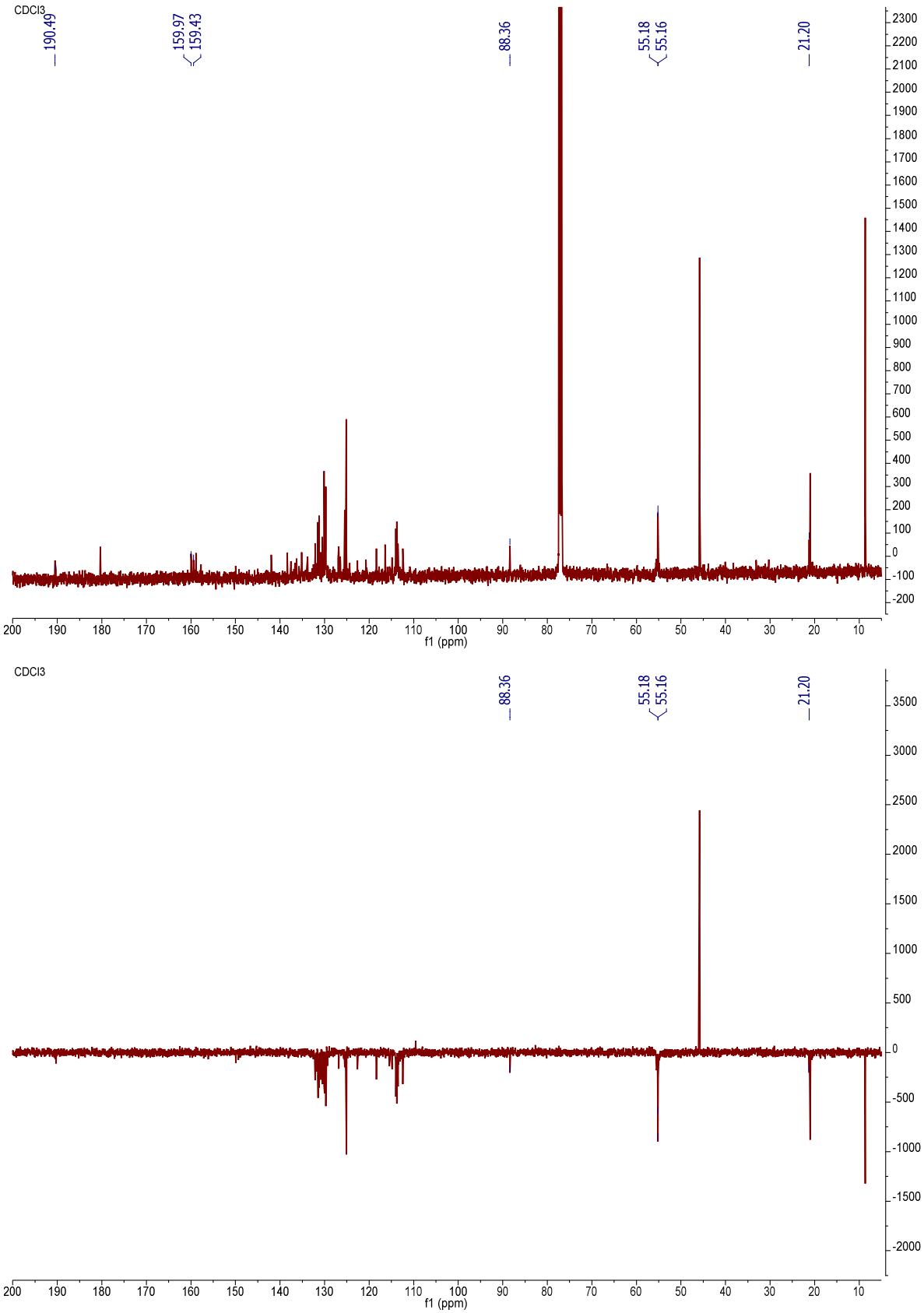
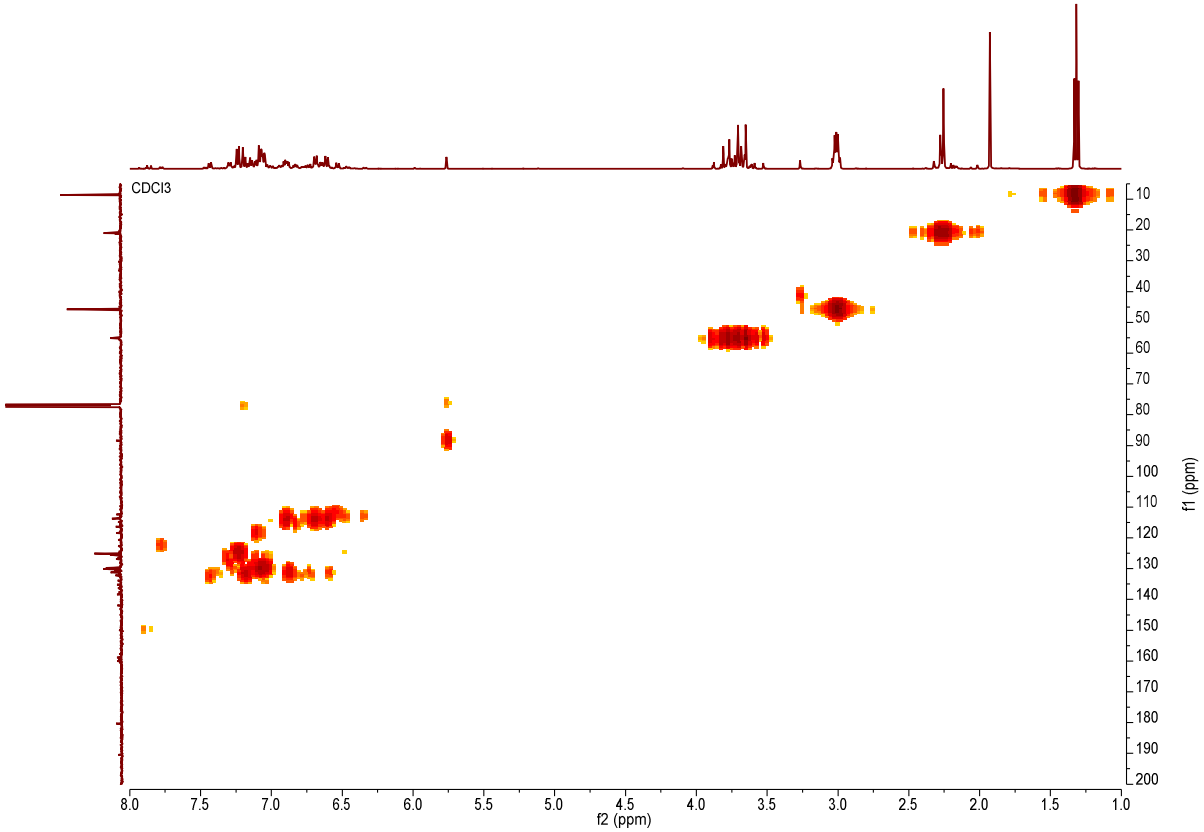
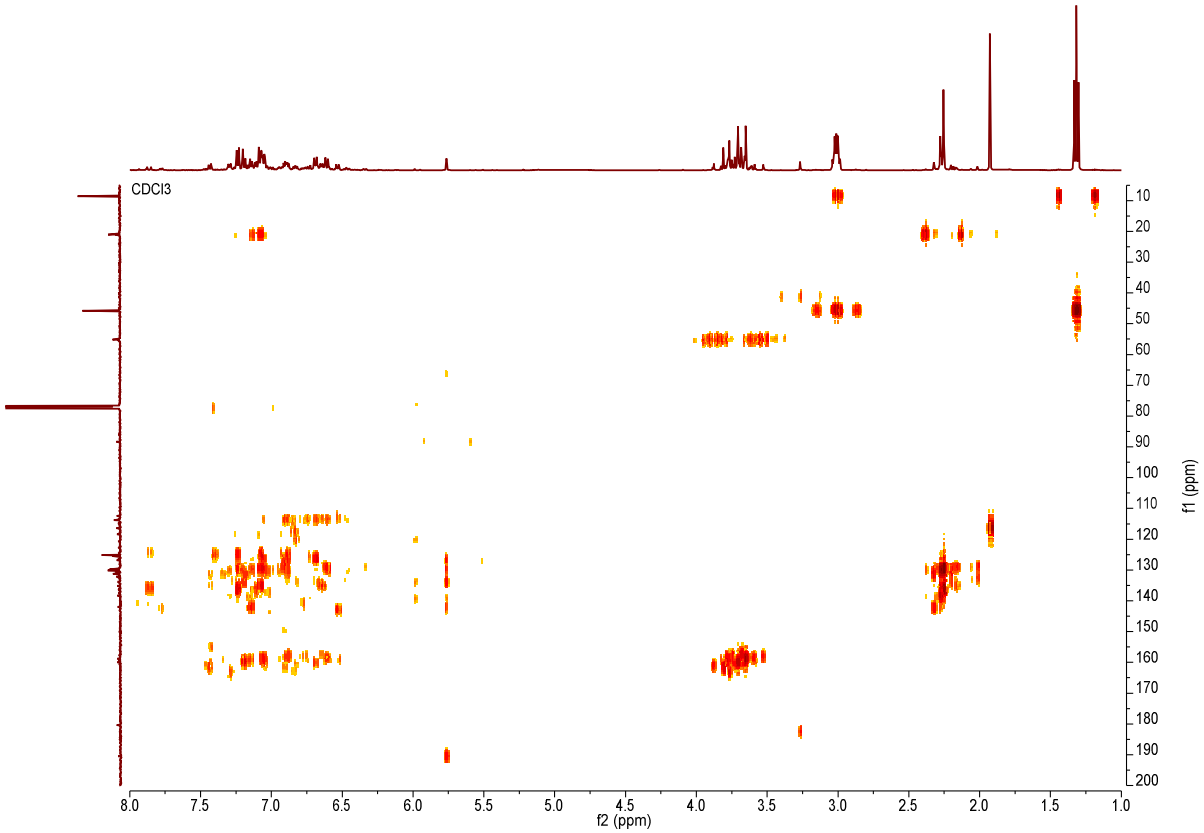

CDCl3
f2 (ppm)
f1 (ppm)

Figure S3. NMR spectra of the crude product of the synthesis of thiazinethione **2v**. Some significant signals belonging to the product structure are marked.




CDCl3
190.49
159.97
159.43
88.36
55.18
55.16
21.20
f1 (ppm)
CDCl3
88.36
55.18
55.16
21.20
f1 (ppm)


CDCl3
f2 (ppm)
f1 (ppm)


CDCl3
f2 (ppm)
f1 (ppm)

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