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Supplementary Information

Cu-Catalyzed Direct C-H Bond Functionalization: A Regioselective Protocol to 5-Aryl Thiazolo[3,2-*b*]-1,2,4-triazoles

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1. Instrumentation and Chemicals

^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX 300 MHz spectrometer in $CDCl_3$ or d_6-DMSO solution. ESI-MS spectra were measured on Finnigan Mat TSQ 7000 instruments. High-resolution electrospray ionization mass spectra (HR-ESI-MS) were recorded on an Agilent 6540Q-TOF LCMS equipped with an electrospray ionization (ESI) probe operating in positive-ion mode with direct infusion. Melting points (mp) were determined with a digital electrothermal apparatus without further correction. Analytical HPLC was performed on a Shimadzu^{TM} LC-10A system via a VP-ODS C18 column (250 mm × 4.6 mm, 5 µm particle size) with a CH_3CN-H_2O mobile phase. TLC analyses were performed on commercial glass plates bearing 0.25-mm layer of Merck Silica gel $60F_{254}$. Silica gel (200-300 mesh) was used for column chromatography. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Solvents were freshly distilled prior to use. Chemical shifts for ^{1}H NMR are expressed in parts per million (ppm) relative to tetramethylsilane (δ 0.0 ppm). Chemical shifts for ^{13}C NMR are expressed in ppm relative to $CDCl_3$ (δ 77.16 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, bs = broad singlet), coupling constant (Hz), and integration. All reactions were carried out under nitrogen atmosphere unless noted.

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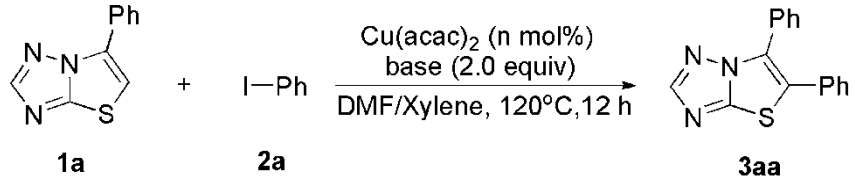
2. Optimization of the Catalyst Loading and Base [a]



1a **2a** **3aa**

entry	catalyst loading (mol%)	base	yield (%)[b]
1	40	*t*-BuOLi	98
2	20	*t*-BuOLi	98
3	10	*t*-BuOLi	87
4	5	*t*-BuOLi	66
5	0	*t*-BuOLi	N.D.[c]
6	20	*t*-BuOK	56
7	20	*t*-BuONa	47
8	20	K_3PO_4	40
9	20	Cs_2CO_3	30
10	20	K_2CO_3	11[d]
11	20	*t*-BuOLi	92[e]
12	20	*t*-BuOLi	trace[f]
13	20	*t*-BuOLi	98[g]

[a] The reaction was performed with **1a** (0.5 mmol), **2a** (1.0 mmol), base (2.0 equiv) and $Cu(acac)_2$ (n mol%) in 1 mL of DMF/Xylene at 120 °C for 12 h. [b] Isolated yield. [c] N.D.: not determined. [d] The yield was estimated by HPLC. Reaction was carried out at 100 °C [e]; r. t [f]; 140 °C [g].

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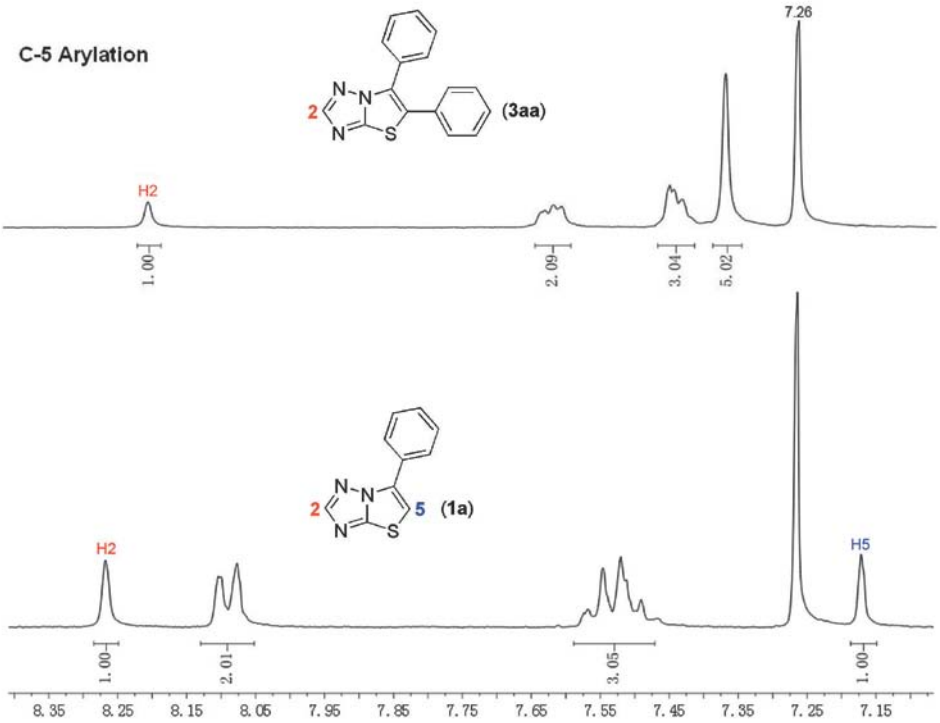
3. Structural Characterization of C-5 Arylation Products by ^{1}H NMR Spectra



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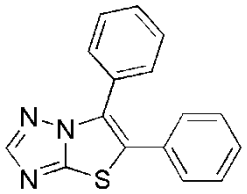
4. Typical Procedure for the Cu-catalyzed Direct Arylation of Thiazolo[3,2-b]-1,2,4-triazoles with Aryl Iodides

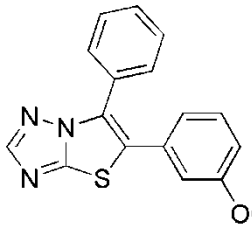
A suspension of thiazolo[3,2-*b*]-1,2,4-triazoles (0.50 mmol), $Cu(acac)_2$ (26 mg, 0.10 mmol, 20 mol %), *t*-BuOLi (80 mg, 1.00 mmol, 2.0 equiv), and aryl iodides (1.00 mmol) in DMF/Xylene (0.5/0.5 mL) was stirred at room temperature for 5 min under N_2 and heated in oil bath (120 ^oC) for 12 h. The reaction mixture was allowed to cool to room temperature and diluted with ethyl acetate (25 mL). The resulting solution was washed with brine (3×10 mL), dried over anhydrous Na_2SO_4 and concentrated under vacuum to a volume of about 2 mL. The mixture containing the product was subjected to flash chromatography on silica gel (ethyl acetate / petroleum ether mixtures) to afford target arylation product.

5. Spectral Data of Products



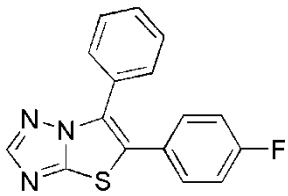
(3aa)

Known compound.[S1] Colorless solid. Yield: 98% (136 mg). Mp: 191-193 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.26 (s, 1H), 7.63-7.60 (m, 2H), 7.44-7.42 (m, 3H), 7.36 (s, 5H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 155.8, 131.2, 129.8, 129.3, 129.1, 128.9, 128.6, 127.9, 127.2. ESI-MS m/z (%) 278.09 (100) $[M+H]^+$. HRMS (ESI) calcd. for $C_{16}H_{11}N_3S$ $[MH^+]$: 278.0746; Found: 278.0749.



(3ab)

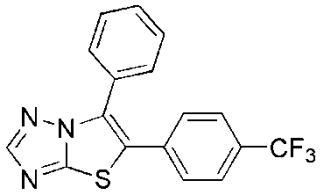
Colorless oil. Yield: 94% (144 mg). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.17 (s, 1H), 7.65-7.62 (m, 2H), 7.45-7.43 (m, 3H), 7.26 (d, J = 15.8 Hz, 1H), 6.96-6.87 (m, 3H), 3.69 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.8, 155.2, 132.3 130.1, 129.8, 128.8, 128.3, 127.8, 127.1, 126.6, 121.5, 114.9, 55.2. ESI-MS m/z (%) 308.05 (100) $[M+H]^+$. HRMS (ESI) calcd. for $C_{17}H_{13}N_3OS$ $[MH^+]$: 308.0852; Found: 308.0856.



(3ac)

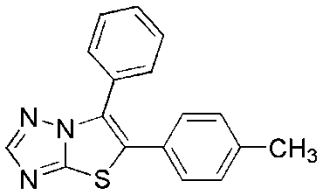
Colorless solid. Yield: 89% (131 mg). Mp: 186-188 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.25 (s, 1H), 7.61-7.58 (m, 2H), 7.45-7.43 (m, 3H), 7.37-7.32 (m, 2H), 7.06 (t, J = 8.5 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 163.0 (J_{CF} = 250.6 Hz), 155.9, 131.3 (J_{CF} = 8.2 Hz), 129.9, 129.7, 128.9, 128.7, 127.7, 127.3, 127.2, 125.9, 116.3

(J_{CF} = 22.0 Hz). ESI-MS m/z (%) 296.05 (100) $[M+H]^+$. HRMS (ESI) calcd. For $C_{16}H_{10}FN_3S$ $[MH^+]$: 296.0652; Found: 296.0655.



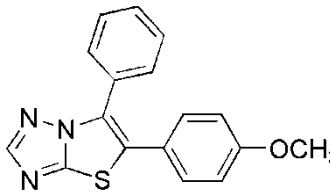
(3ad)

Colorless solid. Yield: 85% (147 mg). Mp: 141-143 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.21 (s, 1H), 7.63-7.59 (m, 4H), 7.50-7.46 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 155.6, 134.9, 130.2, 129.8, 129.6, 129.1, 127.2, 126.1, 126.0, 125.4. ESI-MS m/z (%) 345.95 (100) $[M+H]^+$. HRMS (ESI) calcd. for $C_{17}H_{10}F_3N_3S$ $[MH^+]$: 346.0620; Found: 346.0624.



(3ae)

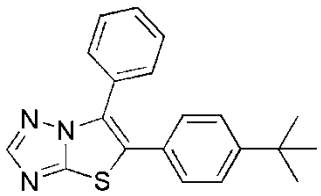
Colorless solid. Yield: 91% (133 mg). Mp: 182-184 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.17 (s, 1H), 7.64-7.61 (m, 2H), 7.44-7.42 (m, 3H), 7.25 (d, J = 8.1 Hz, 2H), 7.15 (d, J = 8.1 Hz, 2H), 2.37 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 155.1, 139.3, 129.8, 129.7, 129.6, 129.2, 128.8, 128.2, 127.9, 127.5, 21.3. ESI-MS m/z (%) 291.95 (100) $[M+H]^+$. HRMS (ESI) calcd. for $C_{17}H_{13}N_3S$ $[MH^+]$: 292.0903; Found: 292.0907.



(3af)

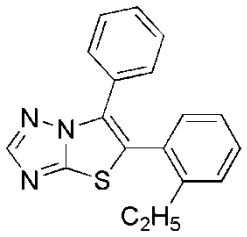
Colorless solid. Yield: 93% (143 mg). Mp: 113-115 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.17 (s, 1H), 7.64-7.61 (m, 2H), 7.44-7.42 (m, 3H), 7.29 (d, J = 8.8 Hz, 2H), 6.88 (d, J = 8.8 Hz, 2H), 3.83 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 160.2, 155.0,

130.7, 129.7, 129.6, 128.8, 127.9, 127.6, 127.3, 123.3, 54.9. ESI-MS m/z (%) 307.95 (100) $[M+H]^+$. HRMS (ESI) calcd. for $C_{17}H_{13}N_3OS$ $[MH^+]$: 308.0852; Found: 308.0856.



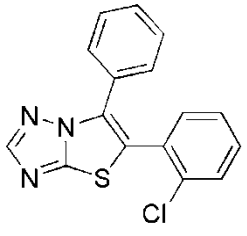
(3ag)

Colorless solid. Yield: 90% (150 mg). Mp: 125-127 ^oC. ^1H NMR (300 MHz, $CDCl_3$): δ 8.17 (s, 1H), 7.66-7.62 (m, 2H), 7.46-7.44 (m, 3H), 7.36 (d, J = 8.6 Hz, 2H), 7.29 (d, J = 8.6 Hz, 2H), 1.32 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 155.1, 154.4, 152.4, 129.8, 129.7, 128.8, 128.2, 127.9, 127.8, 127.5, 126.0, 34.8, 31.2. ESI-MS m/z (%) 334.00 (100) $[M+H]^+$. HRMS (ESI) calcd. for $C_{20}H_{19}N_3S$ $[MH^+]$: 334.1372; Found: 334.1377.



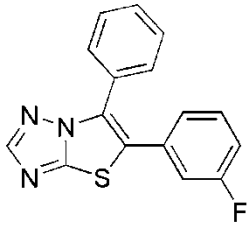
(3ah)

Colorless solid. Yield: 96% (147 mg). Mp: 108-110 ^oC. ^1H NMR (300 MHz, $CDCl_3$): δ 8.23 (s, 1H), 7.60-7.56 (m, 2H), 7.43-7.24 (m, 7H), 2.49 (q, J = 7.5 Hz, 2H), 1.01 (t, J = 7.5 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 155.1, 143.9, 139.4, 132.0, 129.4, 129.2, 128.7, 128.6, 128.4, 127.9, 127.5, 126.3, 125.9, 26.0, 14.8. ESI-MS m/z (%) 306.00 (100) $[M+H]^+$. HRMS (ESI) calcd. for $C_{18}H_{15}N_3S$ $[MH^+]$: 306.1059; Found: 306.1062.



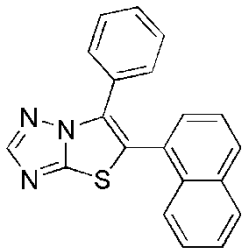
(3ai)

Colorless solid. Yield: 88% (137 mg). Mp: 147-149 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.22 (s, 1H), 7.60-7.56 (m, 2H), 7.50-7.27 (m, 7H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 155.3, 135.1, 133.3, 131.1, 130.4, 129.7, 128.8, 128.7, 127.6, 127.3, 123.4. ESI-MS m/z (%) 311.95 (100) $[M+H]^+$. HRMS (ESI) calcd. for $C_{16}H_{10}ClN_3S$ $[MH^+]$: 312.0357; Found: 312.0359.



(3aj)

Colorless solid. Yield: 82% (121 mg). Mp: 151-153 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.19 (s, 1H), 7.63-7.60 (m, 2H), 7.47-7.45 (m, 3H), 7.34 (dd, J = 14.5, 7.1 Hz, 1H), 7.17-7.05 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 162.8 (J_{CF} = 248.2 Hz), 155.4, 154.5, 133.3, 133.2, 130.8 (J_{CF} = 8.5 Hz), 130.1, 129.7, 129.0, 127.3, 125.6, 125.1 (J_{CF} = 2.6 Hz), 116.2 (J_{CF} = 22.1 Hz). ESI-MS m/z (%) 295.95 (100) $[M+H]^+$. HRMS (ESI) calcd. for $C_{16}H_{10}FN_3S$ $[MH^+]$: 296.0652; Found: 296.0658.



(3ak)

Yellow solid. Yield: 97% (159 mg). Mp: 142-144 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.27 (s, 1H), 7.96-7.89 (m, 3H), 7.60-7.43 (m, 6H), 7.30-7.21 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 155.5, 155.0, 133.7, 132.0, 130.5, 130.3, 129.4, 128.7, 128.5, 127.3, 126.6, 125.4, 125.1. ESI-MS m/z (%) 328.00 (100) $[M+H]^+$. HRMS (ESI) calcd. for $C_{20}H_{13}N_3S$ $[MH^+]$: 328.0903; Found: 328.0906.

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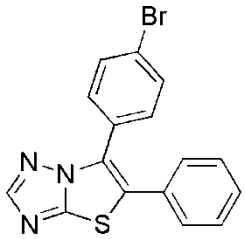
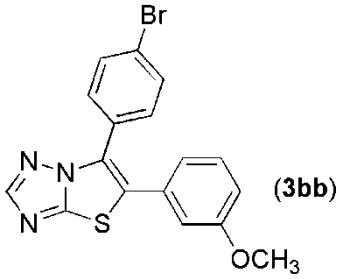


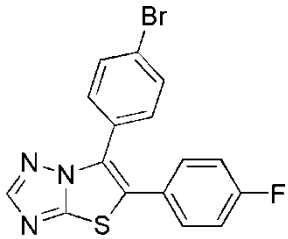
(3ba)

Colorless solid. Yield: 95% (169 mg). Mp: 175-177 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.17 (s, 1H), 7.54 (q, J = 8.6 Hz, 4H), 7.38 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 155.2, 154.7, 138.1, 132.1, 131.2, 130.8, 129.4, 129.3, 129.2, 127.9, 127.2, 127.1, 126.6, 124.1. ESI-MS m/z (%) 355.90 (100) $[M+H]^+$. HRMS (ESI) calcd. for $C_{16}H_{10}BrN_3S$ $[MH^+]$: 355.9852; Found: 355.9852.



(3bb)

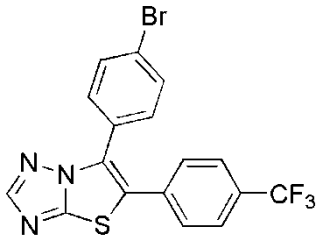
Colorless solid. Yield: 92% (178 mg). Mp: 133-135 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.18 (s, 1H), 7.55 (q, J = 8.9 Hz, 4H), 7.31 (d, J = 8.1 Hz, 1H), 6.95-6.88 (m, 3H), 3.75 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.9, 155.3, 154.6, 138.1, 132.0, 131.2, 130.4, 127.7, 127.0, 126.6, 124.2, 121.7, 114.9, 55.3. ESI-MS m/z (%) 385.90 (100) $[M+H]^+$. HRMS (ESI) calcd. for $C_{17}H_{12}BrN_3OS$ $[MH^+]$: 385.9957; Found: 385.9958.



(3bc)

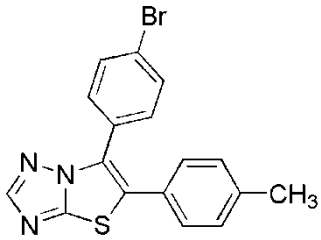
Colorless solid. Yield: 86% (161 mg). Mp: 148-150 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.17 (s, 1H), 7.53 (q, J = 8.5 Hz, 4H), 7.37-7.33 (m, 2H), 7.09 (t, J = 8.4 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 163.2 (J_{CF} = 251.1 Hz), 155.3, 154.5, 138.2,

132.2, 131.3 (J_{CF} = 8.4 Hz), 131.1, 130.1, 127.3, 126.9, 126.6, 126.4, 124.3, 116.6 (J_{CF} = 22.0 Hz), 112.2. ESI-MS m/z (%) 373.90 (100) $[M+H]^+$. HRMS (ESI) calcd. for $C_{16}H_9BrFN_3S$ $[MH^+]$: 373.9757; Found: 373.9759.



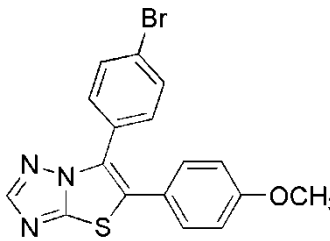
(3bd)

Colorless solid. Yield: 79% (168 mg). Mp: 196-197 ^oC. ^1H NMR (300 MHz, $CDCl_3$): δ 8.22 (s, 1H), 7.63 (q, J = 8.5 Hz, 4H), 7.49 (d, J = 8.5 Hz, 4H), ^{13}C NMR (75 MHz, $CDCl_3$): δ 155.7, 138.4, 134.6, 132.4, 131.2, 129.6, 128.3,126.3, 126.2, 126.1, 125.8, 125.4, 124.7, 121.8. ESI-MS m/z (%) 423.90 (100) $[M+H]^+$. HRMS (ESI) calcd. for $C_{17}H_9BrF_3N_3S$ $[MH^+]$: 423.9725; Found: 423.9723.



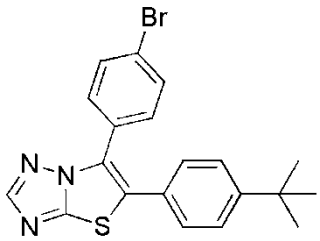
(3be)

Colorless solid. Yield: 90% (167 mg). Mp: 146-148 ^oC. ^1H NMR (300 MHz, $CDCl_3$): δ 8.17 (s, 1H), 7.54 (q, J = 8.7 Hz, 4H), 7.25 (d, J = 8.2 Hz, 2H), 7.18 (d, J = 8.2 Hz, 2H), 2.39 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 155.1, 154.5, 139.6, 138.0, 132.1, 131.2, 129.9, 129.2, 128.1, 127.9, 126.8, 123.9, 21.3. ESI-MS m/z (%) 369.95 (100) $[M+H]^+$. HRMS (ESI) calcd. for $C_{17}H_{12}BrN_3S$ $[MH^+]$: 370.0008; Found: 370.0010.



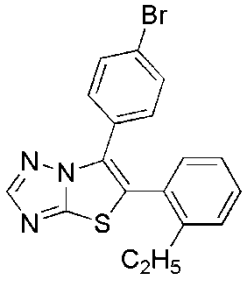
(3bf)

Colorless solid. Yield: 91% (176 mg). Mp: 144-146 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.16 (s, 1H), 7.54 (q, J = 8.6 Hz, 4H), 7.29 (d, J = 8.9 Hz, 2H), 6.90 (d, J = 8.9 Hz, 2H), 3.84 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 160.4, 155.0, 154.4, 138.0, 132.1, 131.1, 130.7, 127.9, 126.8, 126.4, 123.9, 122.9, 114.7, 55.4. ESI-MS m/z (%) 385.95 (100) $[M+H]^+$. HRMS (ESI) calcd. for $C_{17}H_{12}BrN_3OS$ $[MH^+]$: 385.9957; Found: 385.9958.



(3bg)

Colorless solid. Yield: 94% (194 mg). Mp: 168-170 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.17 (s, 1H), 7.55 (q, J = 8.7 Hz, 4H), 7.39 (d, J = 9.1 Hz, 2H), 7.28 (d, J = 9.1 Hz, 2H), 1.34 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 155.2, 154.2, 152.8, 138.1, 132.1, 131.2, 128.9, 127.8, 126.8, 126.7, 126.2, 124.0, 34.8, 31.2. ESI-MS m/z (%) 412.95 (100) $[M+H]^+$. HRMS (ESI) calcd. for $C_{20}H_{18}BrN_3S$ $[MH^+]$: 412.0478; Found: 412.0480.



(3bh)

Colorless solid. Yield: 93% (179 mg). Mp: 132-134 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.21 (s, 1H), 7.51-7.45 (m, 4H), 7.43-7.25 (m, 4H), 2.49 (q, J = 7.6 Hz, 2H), 1.04 (t, J = 7.6 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 155.3, 155.1, 143.9, 137.8, 131.8, 130.0, 129.1, 127.9, 126.8, 126.5, 123.7, 26.1, 14.8. ESI-MS m/z (%) 383.95 (100) $[M+H]^+$. HRMS (ESI) calcd. for $C_{18}H_{14}BrN_3S$ $[MH^+]$: 384.0165; Found: 384.0166.

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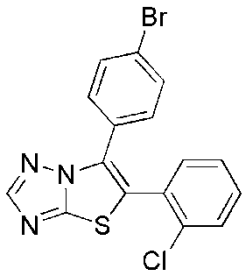
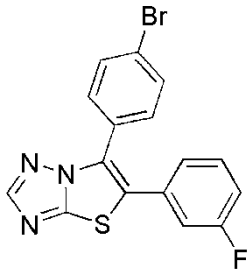


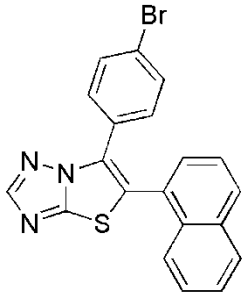
(3bi)

Colorless solid. Yield: 85% (166 mg). Mp: 157-159 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.21 (s, 1H), 7.50 (q, J = 8.6 Hz, 4H), 7.45-7.31 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 155.6, 155.4, 137.9, 135.0, 133.1, 131.4, 130.2, 129.5, 129.2, 127.5, 126.5, 124.1, 123.9. ESI-MS m/z (%) 389.85 (100) $[M+H]^+$. HRMS (ESI) calcd. for $C_{16}H_9BrClN_3S$ $[MH^+]$: 389.9462; Found: 389.9463.



(3bj)

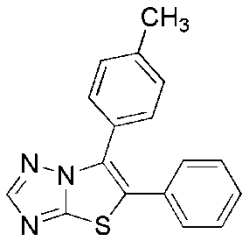
Colorless solid. Yield: 80% (150 mg). Mp: 153-155 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.18 (s, 1H), 7.55 (q, J = 8.6 Hz, 4H), 7.37 (q, J = 7.2 Hz, 1H), 7.16-7.06 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 162.4 (J_{CF} = 248.8 Hz), 155.5, 154.6, 138.2, 132.8, 132.3, 131.2, 131.0 (J_{CF} = 8.6 Hz), 127.7, 126.2, 125.1, 124.5, 116.4 (J_{CF} = 22.0 Hz). ESI-MS m/z (%) 373.90 (100) $[M+H]^+$. HRMS (ESI) calcd. for $C_{16}H_9BrFN_3S$ $[MH^+]$: 373.9757; Found: 373.9758.



(3bk)

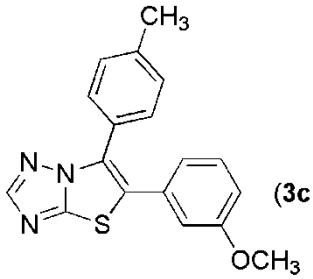
Colorless solid. Yield: 95% (193 mg). Mp: 204-206 ^{o}C. ^{1}H NMR (300 MHz,

$CDCl_3$): δ 8.27 (s, 1H), 8.00-7.85 (m, 3H), 7.58-7.44 (m, 6H), 7.37-7.30 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 155.6, 155.3, 137.7, 133.8, 131.9, 131.8, 130.7, 130.2, 130.0, 128.9, 128.7, 127.7, 127.5, 126.7, 126.6, 125.4, 124.9, 123.8. ESI-MS m/z (%) 405.95 (100) $[M+H]^+$. HRMS (ESI) calcd. for $C_{20}H_{12}BrN_3S$ $[MH^+]$: 406.0008; Found: 406.0008.



(3ca)

Colorless solid. Yield: 98% (143 mg). Mp: 187-189 ^oC. ^1H NMR (300 MHz, $CDCl_3$): δ 8.17 (s, 1H), 7.51 (d, J = 8.1 Hz, 2H), 7.36 (m, 5H), 7.25 (m, 2H), 2.40 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 155.2, 139.9, 131.4, 129.6, 129.3, 129.1, 128.4, 126.6, 124.8, 21.5. ESI-MS m/z (%) 292.00 (100) $[M+H]^+$. HRMS (ESI) calcd. for $C_{17}H_{13}N_3S$ $[MH^+]$: 292.0903; Found: 292.0907.



(3cb)

Colorless solid. Yield: 96% (154 mg). Mp: 117-119 ^oC. ^1H NMR (300 MHz, $CDCl_3$): δ 8.16 (s, 1H), 7.52 (d, J = 8.1 Hz, 2H), 7.29-7.23 (m, 3H), 6.97-6.89 (m, 3H), 3.71 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.8, 155.1, 154.4, 139.9, 132.5, 130.9, 130.1, 129.6, 129.5, 128.8, 128.5, 126.5, 124.8, 121.6, 114.7, 55.2, 21.5. ESI-MS m/z (%) 322.00 (100) $[M+H]^+$. HRMS (ESI) calcd. for $C_{18}H_{15}N_3OS$ $[MH^+]$: 322.1009; Found: 322.1013.

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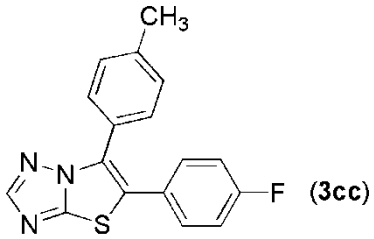
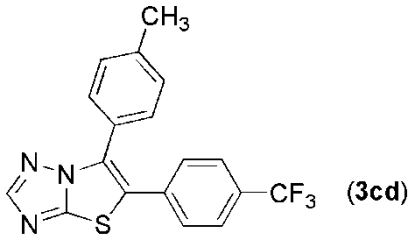


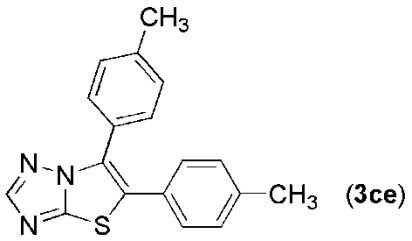
(3cc)

Yellow solid. Yield: 91% (141 mg). Mp: 187-189 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.17 (s, 1H), 7.48 (d, J = 8.0 Hz, 2H), 7.38-7.33 (m, 2H), 7.26-7.23 (m, 2H), 7.06 (t, J = 8.5 Hz, 2H), 2.40 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 163.0 (J_{CF} = 250.4 Hz), 155.2, 154.4, 140.1, 131.2 (J_{CF} = 8.3 Hz), 130.1, 129.7, 129.5, 128.8, 128.5, 127.4, 125.4, 124.5, 116.3 (J_{CF} = 21.9 Hz), 114.1, 21.5. ESI-MS m/z (%) 310.00 (100) $[M+H]^+$. HRMS (ESI) calcd. for $C_{17}H_{12}FN_3S$ $[MH^+]$: 310.0809; Found: 310.0813.



(3cd)

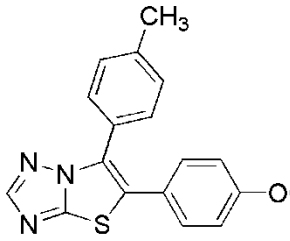
Colorless solid. Yield: 88% (158 mg). Mp: 138-140 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.18 (s, 1H), 7.61 (d, J = 8.1 Hz, 2H), 7.49 (d, J = 8.3 Hz, 4H), 7.27 (d, J = 8.1 Hz, 2H), 2.42 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 155.5, 154.6, 140.5, 135.1, 131.0, 130.6, 129.8, 129.6, 129.5, 126.1, 126.0, 125.5, 124.7, 124.2, 121.9, 114.0, 21.5. ESI-MS m/z (%) 360.00 (100) $[M+H]^+$. HRMS (ESI) calcd. for $C_{18}H_{12}F_3N_3S$ $[MH^+]$: 360.0777; Found: 360.0781.



(3ce)

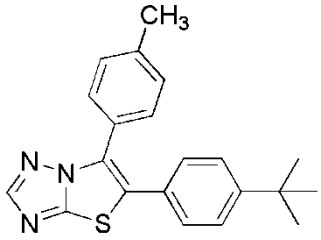
Yellow solid. Yield: 92% (140 mg). Mp: 203-205 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.16 (s, 1H), 7.51 (d, J = 8.1 Hz, 2H), 7.25 (dd, J = 10.7, 5.0 Hz, 4H), 7.15

(d, J = 8.1 Hz, 2H), 2.38 (d, J = 7.9 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 155.1, 139.8, 139.1, 129.8, 129.6, 129.1, 128.4, 128.0, 126.8, 124.9, 114.1, 21.5, 21.3. ESI-MS m/z (%) 306.00 (100) $[M+H]^+$. HRMS (ESI) calcd. for $C_{18}H_{15}N_3S$ $[MH^+]$: 306.1059; Found: 306.1062.



(3cf)

Colorless solid. Yield: 93% (158 mg). Mp: 168-169 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.15 (s, 1H), 7.51 (d, J = 8.5 Hz, 2H), 7.30 (d, J = 8.1 Hz, 2H), 7.23 (d, J = 8.1 Hz, 2H), 6.88 (d, J = 8.5 Hz, 2H), 3.83 (s, 3H), 2.39 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 160.1, 155.0, 139.7, 130.6, 129.5, 126.6, 124.9, 123.5, 114.5, 55.0, 21.5. ESI-MS m/z (%) 322.00 (100) $[M+H]^+$. HRMS (ESI) calcd. for $C_{18}H_{15}N_3OS$ $[MH^+]$: 322.1009; Found: 322.1012.



(3cg)

Colorless solid. Yield: 92% (160 mg). Mp: 119-121 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.15 (s, 1H), 7.52 (d, J = 8.0 Hz, 2H), 7.36 (d, J = 8.5 Hz, 2H), 7.30 (d, J = 8.5 Hz, 2H), 7.25 (d, J = 8.0 Hz, 2H), 2.41 (s, 3H), 1.32 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 155.1, 154.4, 152.3, 139.8, 129.6, 128.8, 128.3, 127.9, 126.9, 126.0, 125.0, 34.8, 31.2, 21.5. ESI-MS m/z (%) 348.05 (100) $[M+H]^+$. HRMS (ESI) calcd. for $C_{21}H_{21}N_3S$ $[MH^+]$: 348.1529; Found: 348.1532.

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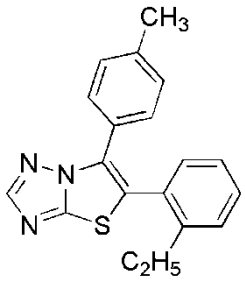
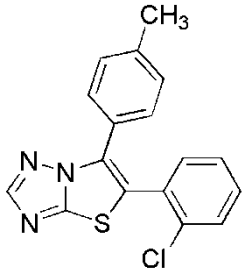


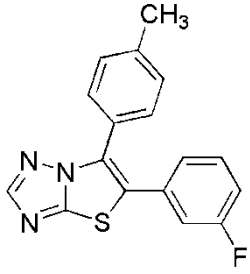
(3ch)

Colorless solid. Yield: 95% (152 mg). Mp: 105-107 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.21 (s, 1H), 7.47 (d, J = 8.2 Hz, 2H), 7.40 (m, 2H), 7.27 (m, 2H), 7.14 (d, J = 8.2 Hz, 2H), 2.49 (q, J = 7.6 Hz, 2H), 2.33 (s, 3H), 1.02 (t, J = 7.6 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 155.1, 144.0, 139.5, 132.1, 130.0, 129.6, 129.3, 129.1, 128.5, 126.3, 125.1, 125.0, 26.1, 21.4, 14.8. ESI-MS m/z (%) 320.05 (100) $[M+H]^+$. HRMS (ESI) calcd. for $C_{19}H_{17}N_3S$ $[MH^+]$: 320.1216; Found: 320.1220.



(3ci)

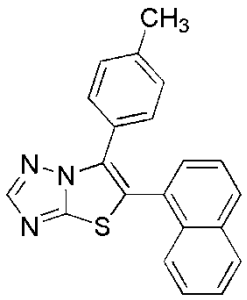
Colorless solid. Yield: 88% (143 mg). Mp: 125-127 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.21 (s, 1H), 7.50-7.36 (m, 5H), 7.31 (dd, J = 7.4, 1.3 Hz, 1H), 7.17 (d, J = 8.0 Hz, 2H), 2.35 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 155.6, 155.3, 139.8, 135.1, 133.3, 131.0, 130.5, 130.3, 130.0, 129.4, 128.7, 127.3, 124.7, 124.0, 122.6, 114.1, 21.4. ESI-MS m/z (%) 326.00 (100) $[M+H]^+$. HRMS (ESI) calcd. for $C_{17}H_{12}ClN_3S$ $[MH^+]$: 326.0513; Found: 326.0517.



(3cj)

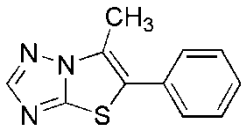
Colorless solid. Yield: 83% (128 mg). Mp: 148-150 ^{o}C. ^{1}H NMR (300 MHz,

$CDCl_3$): δ 8.17 (s, 1H), 7.49 (d, J = 8.6 Hz, 2H), 7.37-7.25 (m, 3H), 7.16 (d, J = 6.9 Hz, 1H), 7.07 (d, J = 8.6 Hz, 2H), 2.41 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 162.8 (J_{CF} = 248.1 Hz), 155.4, 154.6, 140.4, 133.5, 133.4, 130.8 (J_{CF} = 8.2 Hz), 129.8, 129.6, 129.1, 125.0, 124.4, 116.2 (J_{CF} = 21.9 Hz), 21.5. ESI-MS m/z (%) 310.00 (100) $[M+H]^+$. HRMS (ESI) calcd. for $C_{17}H_{12}FN_3S$ $[MH^+]$: 310.0809; Found: 310.0813.



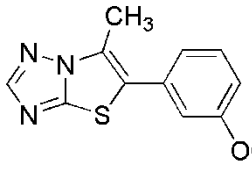
(3ck)

Colorless solid. Yield: 96% (164 mg). Mp: 142-144 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.25 (s, 1H), 7.96-7.90 (m, 3H), 7.59-7.44 (m, 6H), 7.03 (d, J = 7.9 Hz, 2H), 2.26 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 155.6, 155.2, 139.5, 133.7, 132.2, 130.3, 129.2, 128.6, 128.3, 127.2, 126.5,, 125.4, 125.2, 124.8, 124.5, 124.0, 119.1, 114.1, 21.3. ESI-MS m/z (%) 342.05 (100) $[M+H]^+$. HRMS (ESI) calcd. for $C_{21}H_{15}N_3S$ $[MH^+]$: 342.1059; Found: 342.1065.



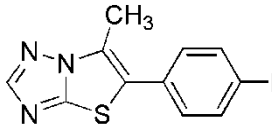
(3da)

Colorless oil. Yield: 90% (97 mg). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.17 (s, 1H), 7.50-7.42 (m, 5H), 2.64 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 155.2, 154.5, 131.1, 130.9, 129.1, 129.0, 128.9, 125.6, 125.1, 114.1, 11.7. ESI-MS m/z (%) 216.00 (100) $[M+H]^+$. HRMS (ESI) calcd. for $C_{11}H_9N_3S$ $[MH^+]$: 216.0590; Found: 216.0591.



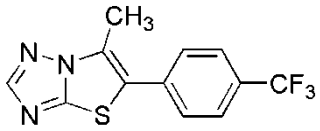
(3db)

Colorless solid. Yield: 98% (120 mg). Mp: 105-106 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.18 (s, 1H), 7.41 (t, J = 7.9 Hz, 1H), 7.07 (d, J = 7.5 Hz, 1H), 6.99 (d, J = 9.6 Hz, 2H), 3.87 (s, 3H), 2.66 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 160.0, 155.3, 132.3, 130.3, 125.4, 125.3, 121.4, 114.9, 114.3, 114.1, 55.4, 11.8. ESI-MS m/z (%) 246.00 (100) $[M+H]^+$. HRMS (ESI) calcd. for $C_{12}H_{11}N_3OS$ $[MH^+]$: 246.0696; Found: 246.0698.



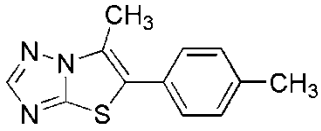
(3dc)

Colorless solid. Yield: 83% (97 mg). Mp: 94-96 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.17 (s, 1H), 7.49-7.45 (m, 2H), 7.20 (t, J = 8.5 Hz, 2H), 2.61 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 163.0 (J_{CF} = 250.2 Hz), 155.2, 154.3, 131.0 (J_{CF} = 8.4 Hz), 127.1, 125.3, 124.4, 116.3 (J_{CF} = 21.9 Hz), 11.5. ESI-MS m/z (%) 234.00 (100) $[M+H]^+$. HRMS (ESI) calcd. for $C_{11}H_8FN_3S$ $[MH^+]$: 234.0496; Found: 234.0495.



(3dd)

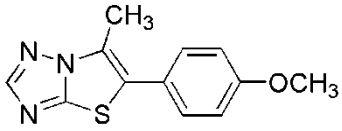
Colorless solid. Yield: 76% (108 mg). Mp: 120-122 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.20 (s, 1H), 7.77 (d, J = 8.2 Hz, 2H), 7.62 (d, J = 8.2 Hz, 2H), 2.68 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 155.7, 134.8, 131.2, 130.7, 129.3, 126.3, 126.2, 126.1, 123.9, 122.0, 114.1, 11.8. ESI-MS m/z (%) 284.00 (100) $[M+H]^+$. HRMS (ESI) calcd. for $C_{12}H_8F_3N_3S$ $[MH^+]$: 284.0464; Found: 284.0468.



(3de)

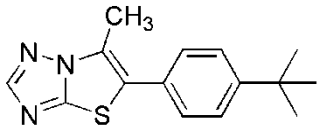
Colorless solid. Yield: 93% (107 mg). Mp: 103-105 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.17 (s, 1H), 7.38 (d, J = 8.1 Hz, 2H), 7.30 (d, J = 8.1 Hz, 2H), 2.63 (s, 3H),

2.43 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 155.2, 139.1, 129.8, 128.9, 128.0, 125.7, 124.4, 123.5, 114.1, 21.3, 11.7. ESI-MS m/z (%) 230.00 (100) $[M+H]^+$. ESI-MS m/z (%) 284.00 (100) $[M+H]^+$. HRMS (ESI) calcd. for $C_{12}H_{11}N_3S$ $[MH^+]$: 230.0746; Found: 230.0748.



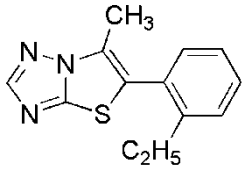
(3df)

Colorless solid. Yield: 92% (113 mg). Mp: 102-104 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.16 (s, 1H), 7.41 (d, J = 8.7 Hz, 2H), 7.01 (d, J = 8.7 Hz, 2H), 3.88 (s, 3H), 2.61 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 160.1, 155.1, 139.3, 130.4, 125.5, 124.4, 123.5, 123.3, 114.6, 55.4, 11.6. ESI-MS m/z (%) 246.00 (100) $[M+H]^+$. HRMS (ESI) calcd. for $C_{12}H_{11}N_3OS$ $[MH^+]$: 246.0696; Found: 246.0699.



(3dg)

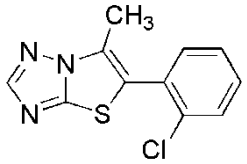
Colorless solid. Yield: 99% (134 mg). Mp: 109-111 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.17 (s, 1H), 7.51 (d, J = 8.4 Hz, 2H), 7.42 (d, J = 8.4 Hz, 2H), 2.65 (s, 3H), 1.37 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 155.2, 152.2, 128.7, 128.2, 126.1, 125.7, 124.8, 114.1, 34.8, 31.2, 11.7. ESI-MS m/z (%) 272.00 (74) $[M+H]^+$. HRMS (ESI) calcd. for $C_{15}H_{17}N_3S$ $[MH^+]$: 272.1216; Found: 272.1218.



(3dh)

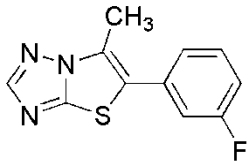
Colorless oil. Yield: 94% (114 mg). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.18 (s, 1H), 7.46-7.36 (m, 2H), 7.31 (t, J = 7.1 Hz, 2H), 2.64 (q, J = 7.5 Hz, 2H), 2.38 (s, 3H), 1.17 (t, J = 7.5 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 155.1, 144.6, 131.9, 130.1,

129.0, 128.7, 126.1, 124.0, 114.1, 26.3, 15.4, 11.2. ESI-MS m/z (%) 244.00 (100) $[M+H]^+$. HRMS (ESI) calcd. for $C_{13}H_{13}N_3S$ $[MH^+]$: 244.0903; Found: 244.0907.



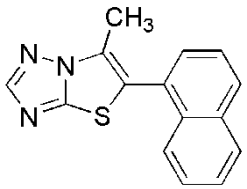
(3di)

Colorless oil. Yield: 87% (109 mg). ^{1}H NMR (300 MHz, $CDCl_3$):δ 8.18 (s, 1H), 7.55 (d, J = 8.3 Hz, 1H), 7.47-7.35 (m, 3H), 2.44 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 155.3, 135.1, 133.0, 131.1, 130.3, 129.2, 127.5, 127.2, 121.7, 114.1, 11.6. ESI-MS m/z (%) 249.95 (100) $[M+H]^+$. HRMS (ESI) calcd. for $C_{11}H_8ClN_3S$ $[MH^+]$: 250.0200; Found: 250.0202.



(3dj)

Colorless solid. Yield: 81% (94 mg). Mp: 114-116 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.18 (s, 1H), 7.51-7.44 (m, 1H), 7.29-7.12 (m, 3H), 2.66 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 162.9 (J_{CF} = 248.4 Hz), 155.4, 154.4, 130.9 (J_{CF} = 8.6 Hz), 125.8, 124.8, 116.2, 116.0 (J_{CF} = 22.0 Hz), 114.1, 11.7. ESI-MS m/z (%) 234.00 (100) $[M+H]^+$. HRMS (ESI) calcd. for $C_{11}H_8FN_3S$ $[MH^+]$: 234.0496; Found: 234.0499.



(3dk)

Yellow oil. Yield: 93% (123 mg). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.23 (s, 1H), 8.02-7.95 (m, 2H), 7.86 (d, J = 9.2 Hz, 1H), 7.62-7.55 (m, 4H), 2.40 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 155.4, 155.2, 133.7, 132.2, 130.3, 130.0, 128.7, 127.5, 127.3, 127.1, 126.6, 125.2, 125.0, 122.8, 114.1, 11.6. ESI-MS m/z (%) 266.05 (100) $[M+H]^+$. HRMS (ESI) calcd. for $C_{15}H_{11}N_3S$ $[MH^+]$: 266.0746; Found: 266.0748.

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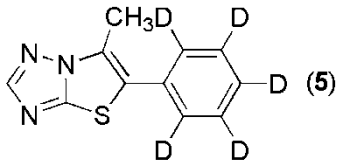

(**5**)

Colorless solid. Yield: 88% (97 mg). Mp: 82-83 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.17 (s, 1H), 2.64 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 155.2, 130.9, 128.9, 128.8, 128.4, 128.3, 128.1, 125.4, 125.0, 114.1, 11.7. ESI-MS m/z (%) 221.05 (100) $[M+H]^+$. HRMS (ESI) calcd. for $C_{11}H_4D_5N_3S$ $[MH^+]$: 221.0904; Found: 221.0906.

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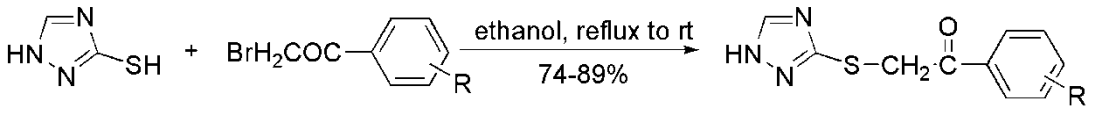
6. Synthesis and Spectral Data of Substrate



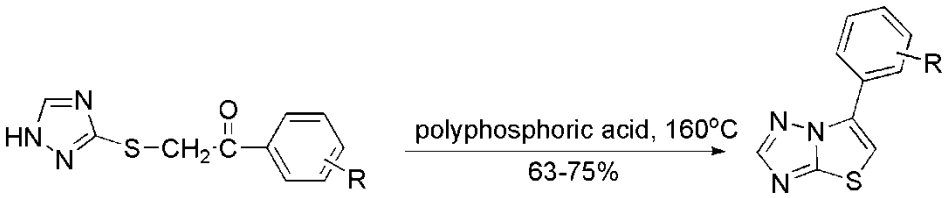
S1: R= H; **S2**: R= Br; **S3**: R= CH_3

To a stirred solution of 3-mercapto-1,2,4-triazole (5.00 g, 50.0 mmol) in ethanol (250 mL) was added 2-bromoacetophenone or its derivatives (50.0 mmol) and the mixture stirred under reflux for 2 h and at room temperature for 12 h. The precipitated product was filtered and recrystallized from water to give pure white solid.[S2]

2-(1*H*-1,2,4-triazol-3-ylthio)-1-phenylethanone **(S1)** (9.10 g, 83%). ^{1}H NMR (300 MHz, d_6-DMSO) δ 8.41 (s, 1H), 8.02-7.99 (m, 2H), 7.69-7.64 (m, 1H). 7.56-7.51 (m, 2H), 4.81 (s, 2H).

2-(1*H*-1,2,4-triazol-3-ylthio)-1-(4-bromophenyl) ethanone **(S2)** (13.27 g, 89%). ^{1}H NMR (300 MHz, d_6-DMSO) δ 8.40 (s, 1H), 7.94 (d, J = 8.6 Hz, 2H), 7.76 (d, J = 8.6 Hz, 2H), 4.77 (s, 2H);

2-(1*H*-1,2,4-triazol-3-ylthio)-1-*p*-tolylethanone **(S3)** (8.63 g, 74%). ^{1}H NMR (300 MHz, d_6-DMSO) δ 8.40 (s, 1H), 7.90 (d, J = 8.2 Hz, 2H), 7.34 (d, J = 8.1 Hz, 2H), 4.77 (s, 2H), 2.38 (s, 2H).



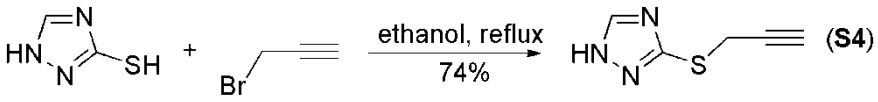
S1: R= H; **S2**: R= Br; **S3**: R= CH_3 **1a**: R= H; **1b**: R= Br; **1c**: R= CH_3

The mixture of 2-(1*H*-1,2,4-triazol-3-ylthio)-1-phenylethanone **S1** (2.00 g, 9.1 mmol) and polyphosphoric acid (8.00 g, 23.7 mmol) was heated at 160 ^{o}C for 3 h. Then an aqueous solution of sodium hydrogen carbonate was added and the crude product was extracted twice by ethyl acetate. The extracts were washed

with water and dried over anhydrous sodium sulfate. After removing of the solvent under reduced pressure, the residue was crystallized from petroleum ether to give pure white solid 6-phenylthiazolo[3,2-*b*]-1,2,4-triazole (**1a**).[S2] Yield: 1.32 g (72%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.27 (s, 1H), 8.09 (d, J = 6.9 Hz, 2H), 7.57-7.47 (m, 3H), 7.17 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 157.2, 156.0, 133.1, 129.8, 129.0, 127.9, 126.6, 108.5. ESI-MS m/z (%) 202.05 (100) $[M+H]^+$.

6-(4-bromophenyl)thiazolo[3,2-*b*]-1,2,4-triazole (**1b**) The compound was prepared from **S2** (2.00 g, 6.7 mmol) and polyphosphoric acid (5.88 g, 17.4 mmol), and using the general procedure described above for **1a**. White solid. Yield: 1.18 g (63%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.27 (s, 1H), 8.01 (d, J = 8.4 Hz, 2H), 7.67 (d, J = 5.7 Hz, 2H), 7.18 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 157.2, 156.1, 132.2, 128.3, 128.0, 126.8, 124.1, 109.0. ESI-MS m/z (%) 279.95 (100) $[M+H]^+$.

6-*p*-tolylthiazolo[3,2-*b*]-1,2,4-triazole (**1c**) The compound was prepared from **S3** (2.00 g, 8.6 mmol) and polyphosphoric acid (7.57 g, 22.4 mmol), and using the general procedure described above for **1a**. White solid. Yield: 1.39 g (75%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.24 (s, 1H), 7.98 (d, J = 8.2 Hz, 2H), 7.34(d, J = 8.0 Hz, 2H), 7.09 (s, 1H), 2.43 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 157.1, 155.9, 140.1, 133.3, 129.7, 126.5, 125.1, 107.6, 21.4. ESI-MS m/z (%) 216.06 (100) $[M+H]^+$.



To a stirred solution of 3-mercapto-1,2,4-triazole (2.02 g, 20.0 mmol) in ethanol (150 mL), prop-2-ynyl bromide (1.8 mL, 20.0 mmol) was added dropwise and The mixture was refluxed for 3 h. After evaporation of solvent under reduced pressure, the residue was poured onto crushed ice. The solid was isolated by filtration and crystallized from ethanol to give pure white solid.[S3]

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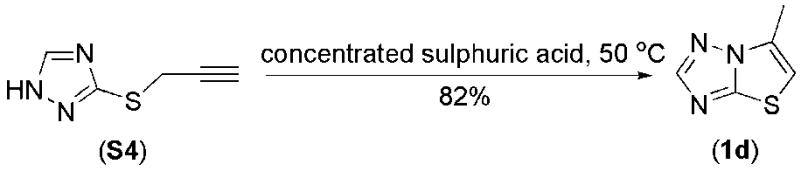
3-(prop-2-ynylthio)-1*H*-1,2,4-triazole (**S4**) (2.15 g, 77%). ^{1}H NMR (300 MHz, d_6-DMSO) δ 8.58 (s, 1H), 3.93 (d, J = 2.5 Hz, 2H), 3.15 (t, J = 2.1 Hz, 1H).



(**S4**) (**1d**)

The mixture of 3-(prop-2-ynylthio)-1*H*-1,2,4-triazole (**S4**) (2.10 g, 15.1 mmol) and concentrated sulphuric acid (15 mL) was kept at 50 ^{o}C for 50 min, then cooled , poured onto crushed ice, filtered and the residue was crystallized from ethanol to give white solid 6-methylthiazolo[3,2-*b*]-1,2,4-triazole (**1d**).[S3] Yield: 1.72 g (82%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.16 (s, 1H), 6.64 (s, 1H), 2.56 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 156.3, 156.1, 129.6, 107.6, 12.5. ESI-MS m/z (%) 140.00 (100) $[M+H]^+$.

Reference:

(S1) Manivannan, E.; Prasanna, S.; Chaturvedi, S. C. *Ind. J. Biochem. Bio*. **2004**, *41*, 179.

(S2) Henichart, J. P.; Houssin, R.; Bernier, J. L. *J. Heterocycl. Chem*. **1986**, *23*, 1531.

(S3) Heravi, M. M.; Tajbakhsh, M.; Rahimizadeh, M.; Davoodnia, A.; Aghapoor, K. *Synth. Commun*. **1999**, *29*, 4417.

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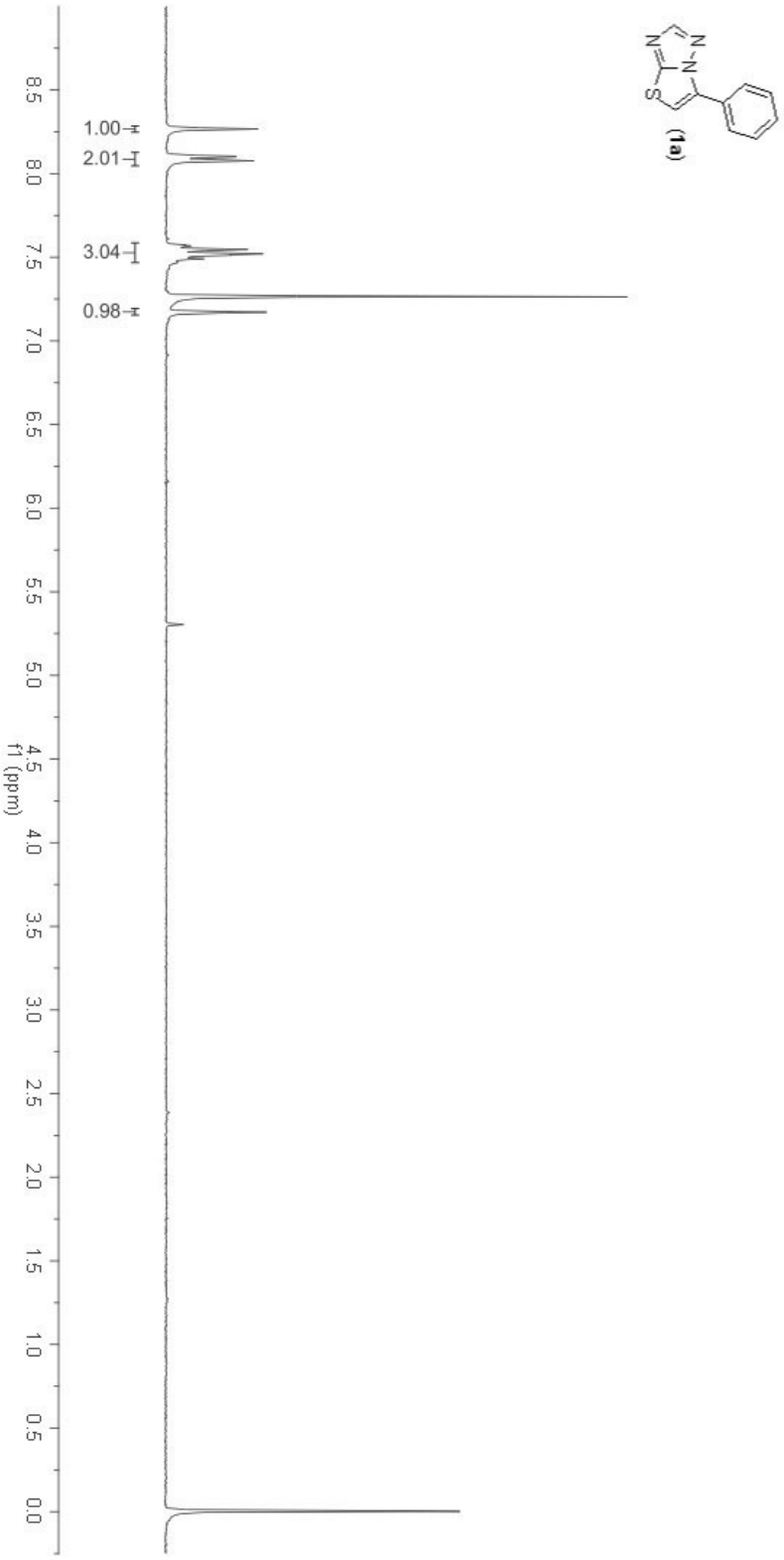
[^{1}H NMR Spectra of **1a**]



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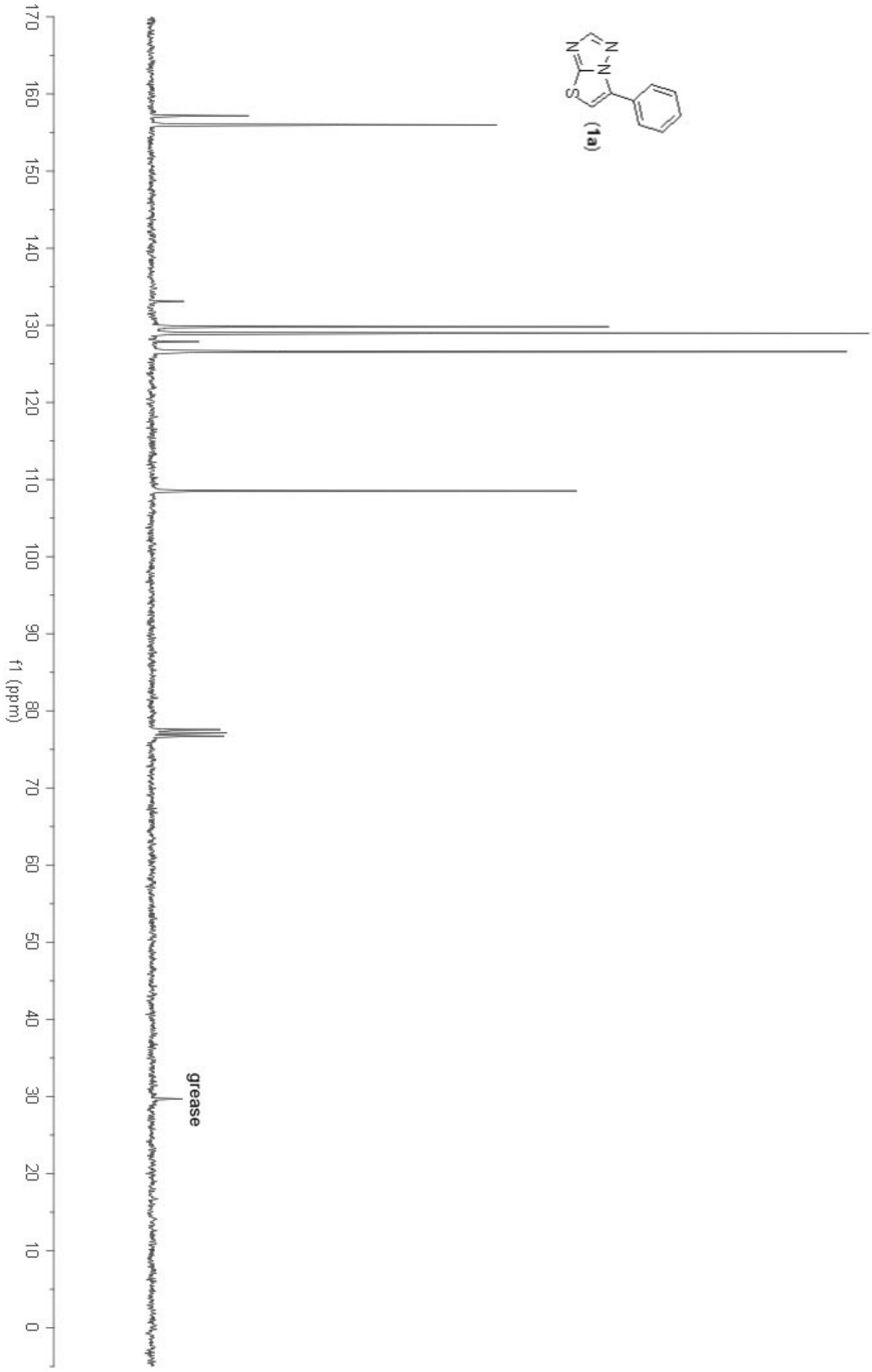
[^{13}C NMR Spectra of **1a**]



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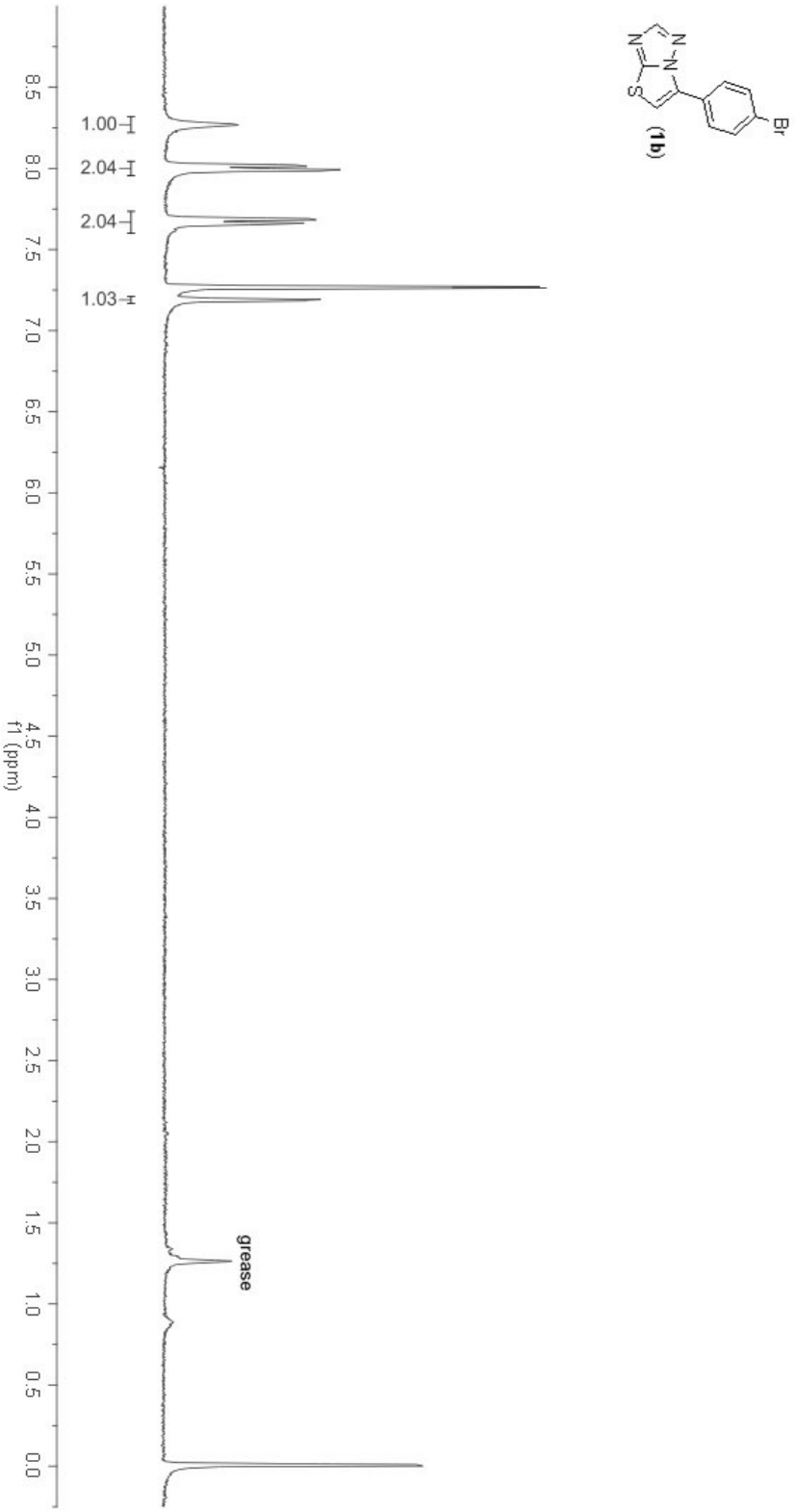
[^{1}H NMR Spectra of **1b**]



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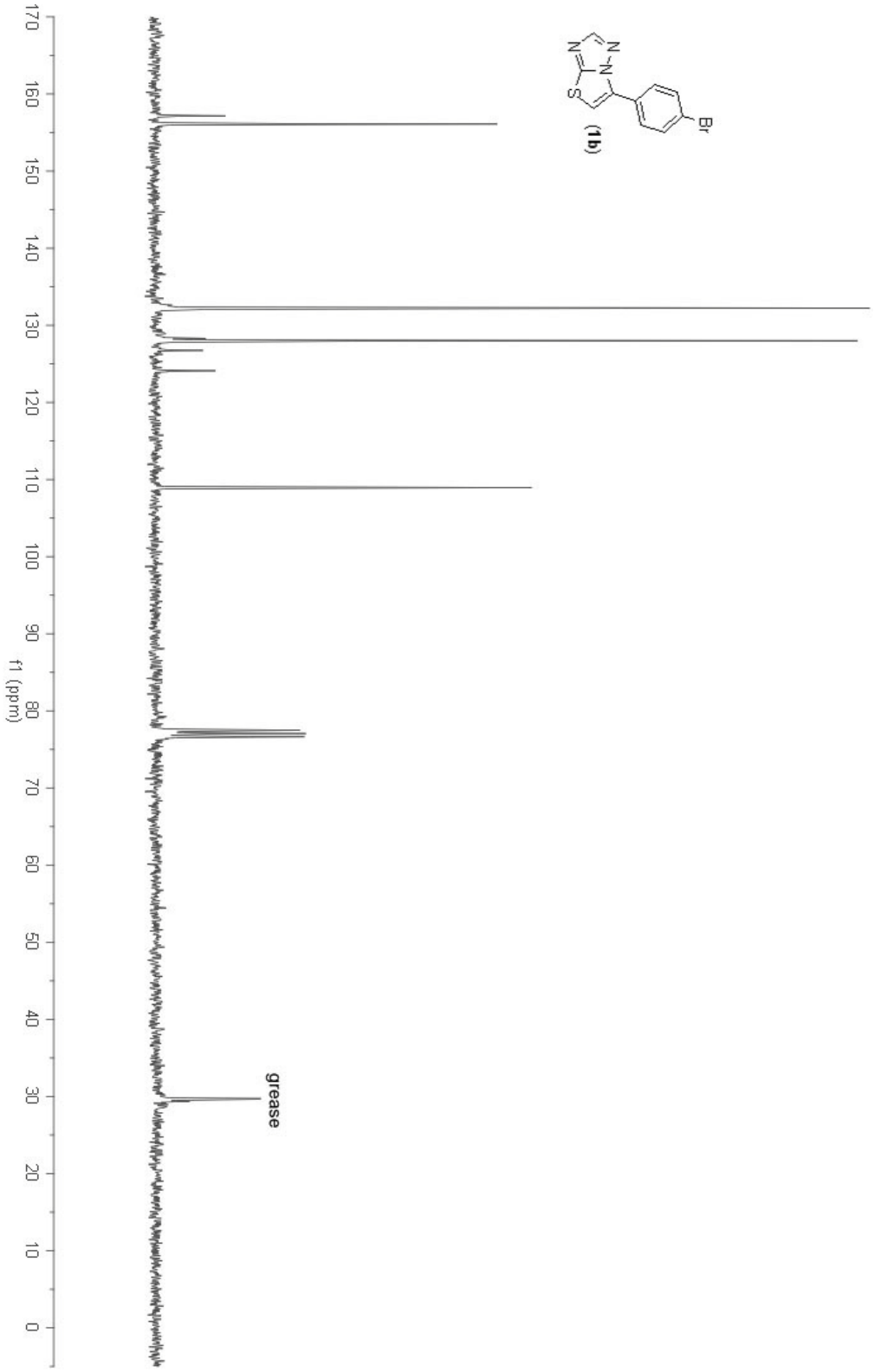
[^{13}C NMR Spectra of **1b**]



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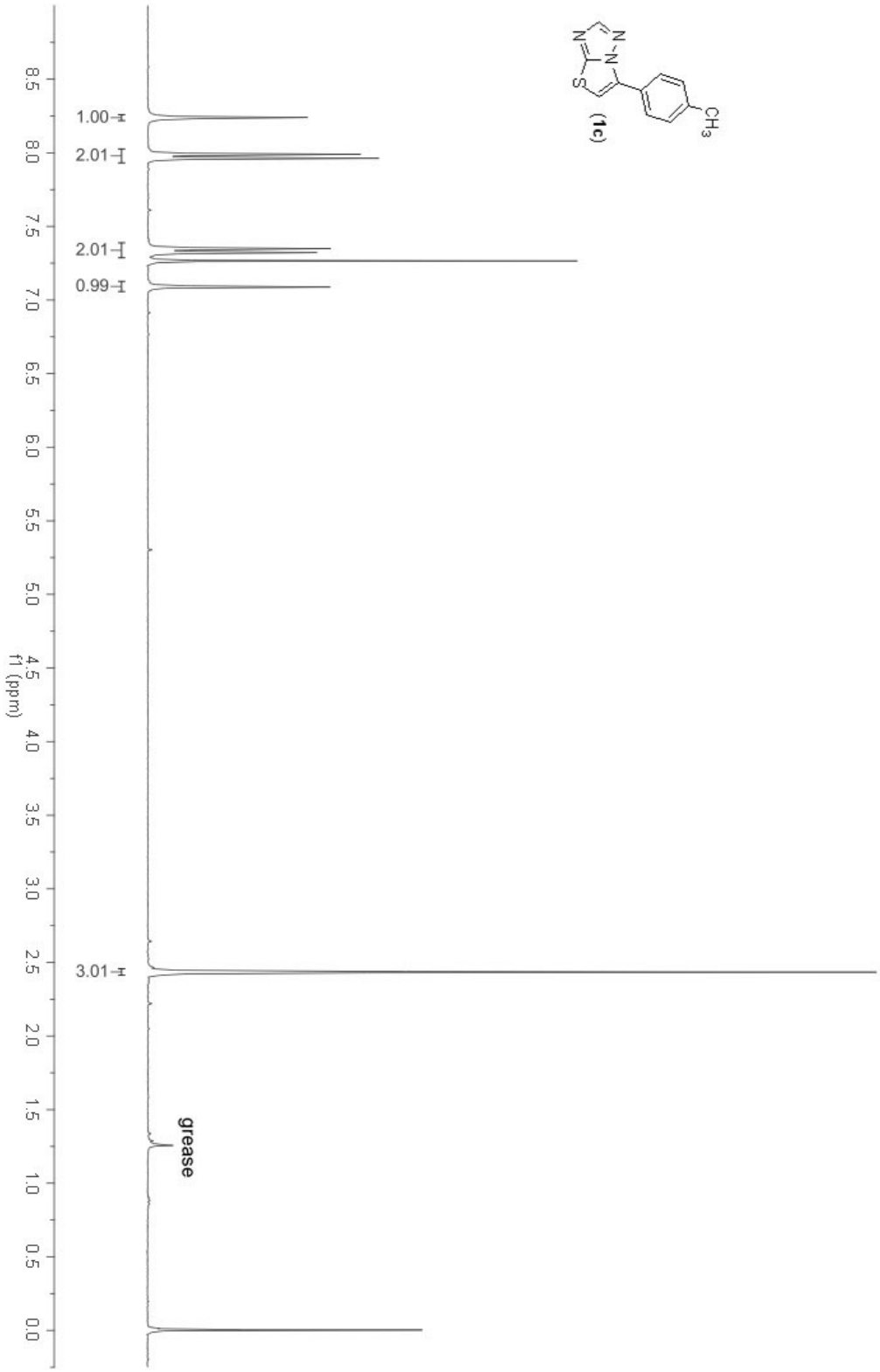
[^{1}H NMR Spectra of **1c**]



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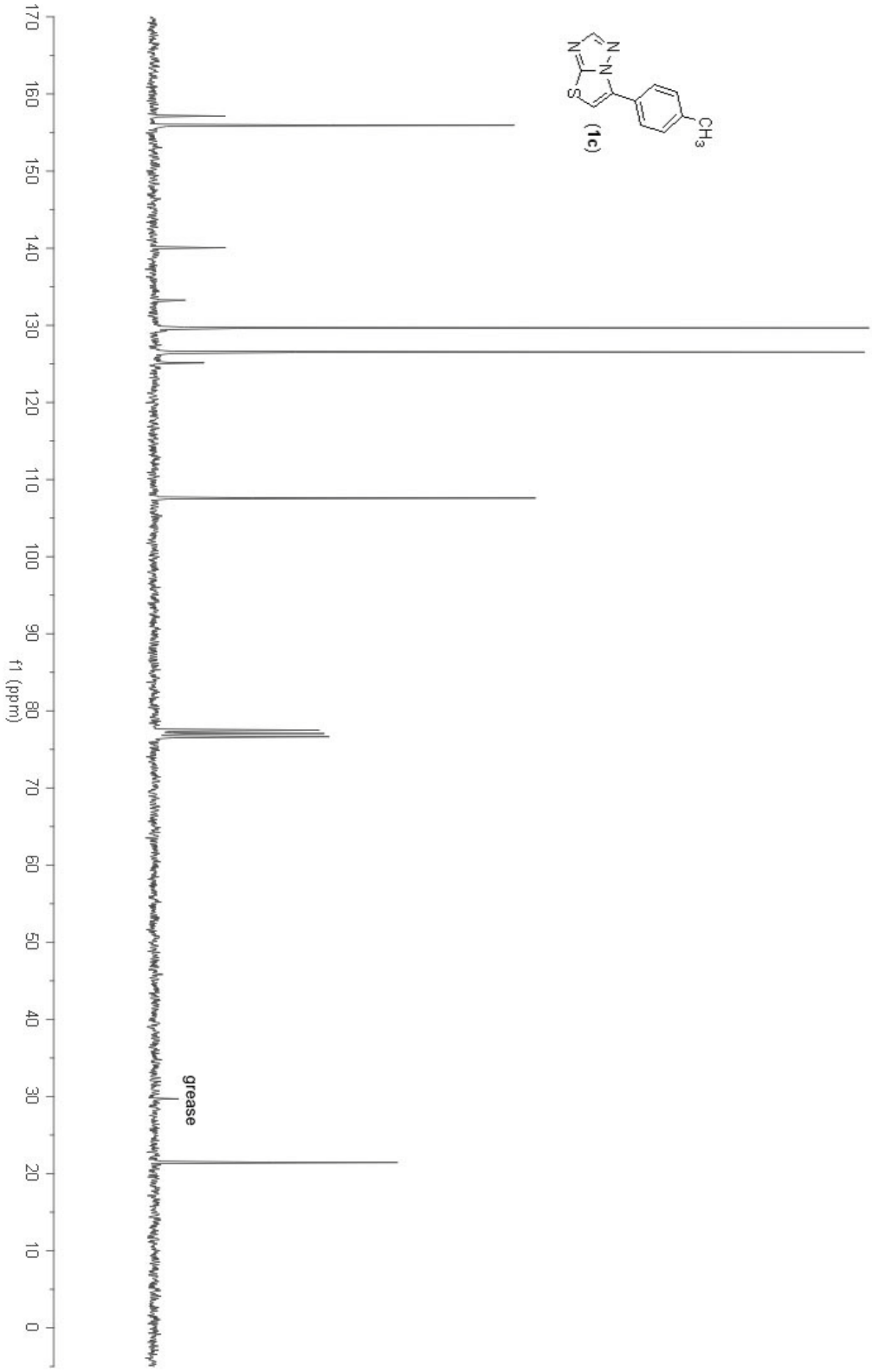
[^{13}C NMR Spectra of **1c**]



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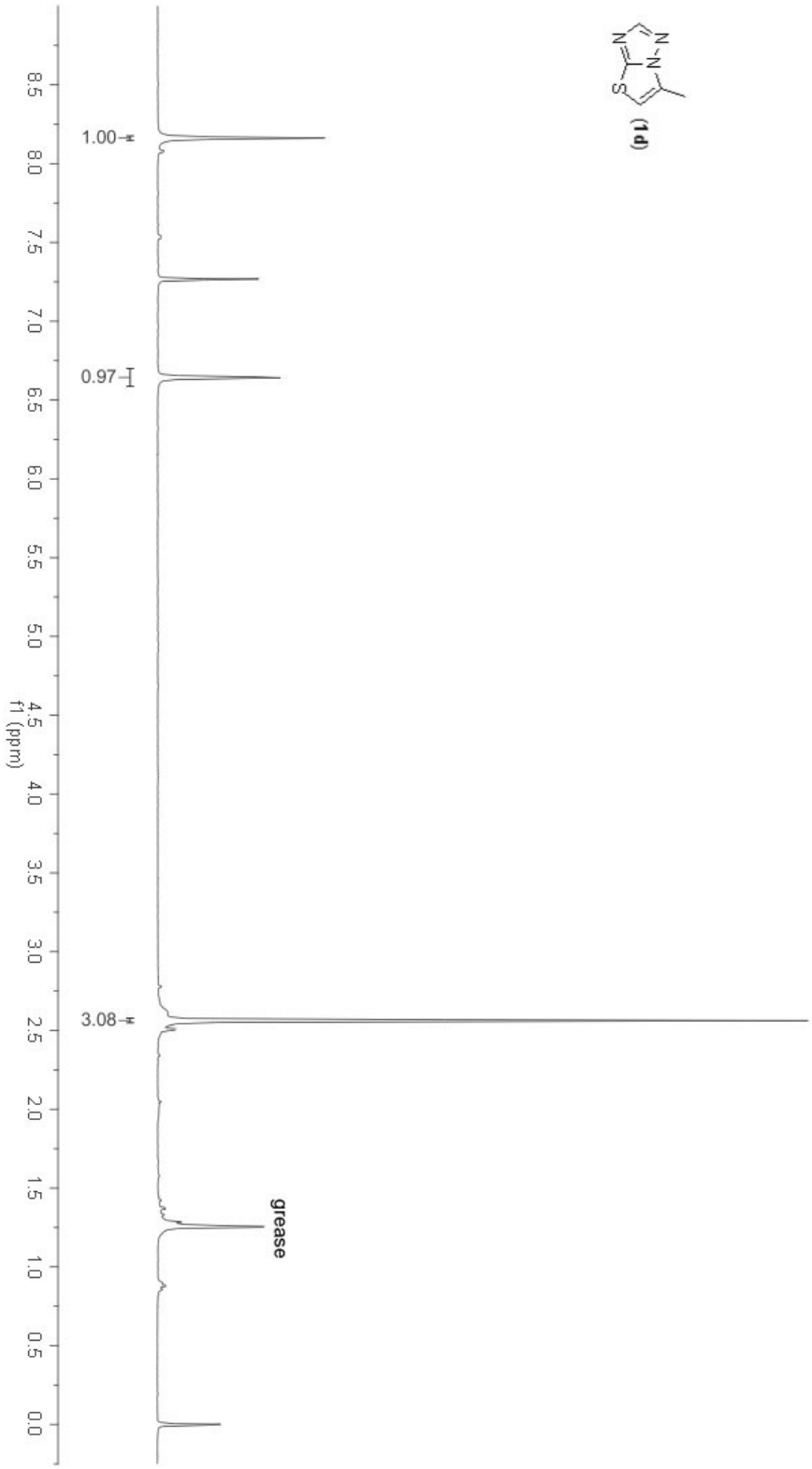
[^{1}H NMR Spectra of **1d**]



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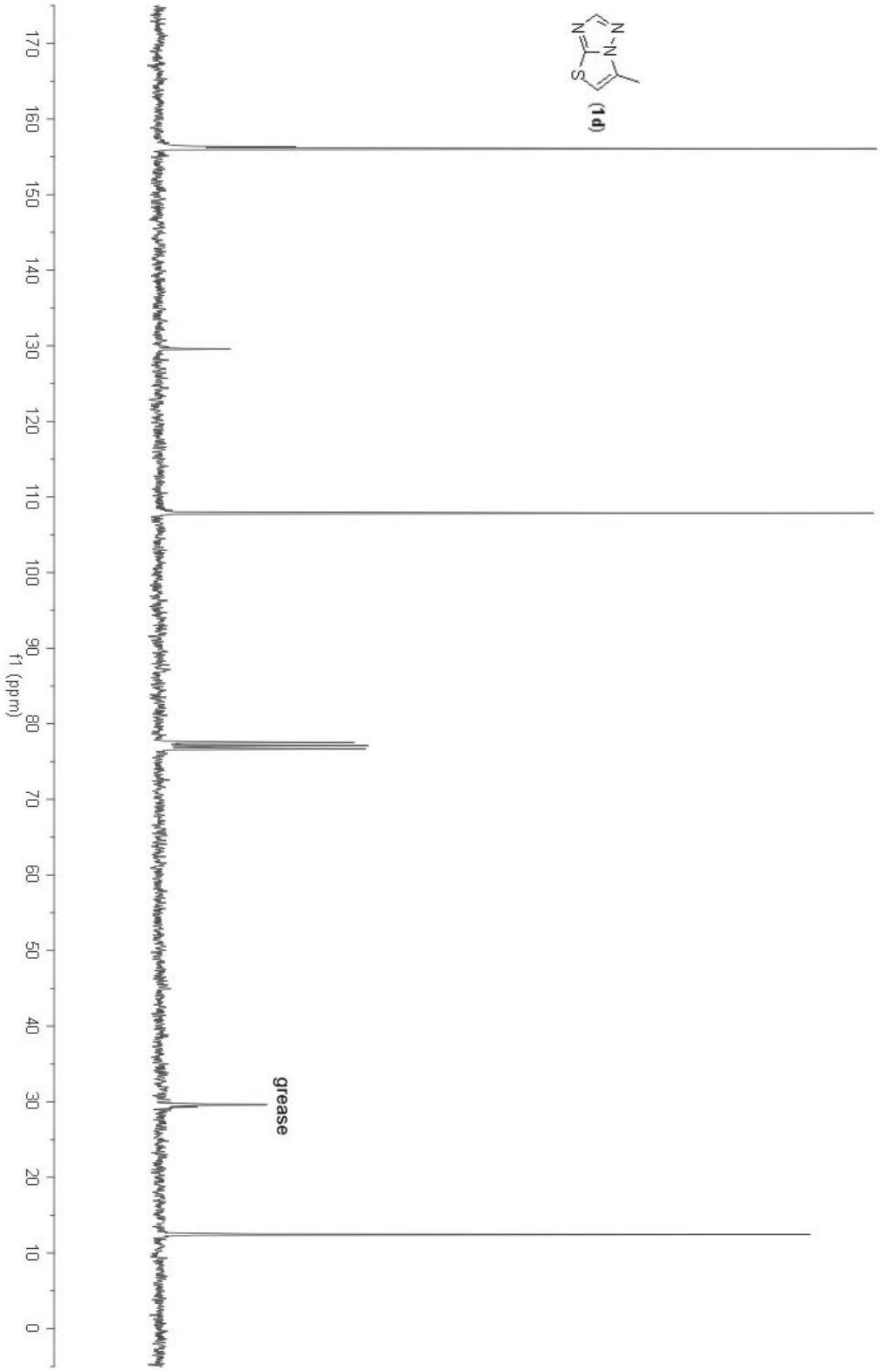
[^{13}C NMR Spectra of **1d**]



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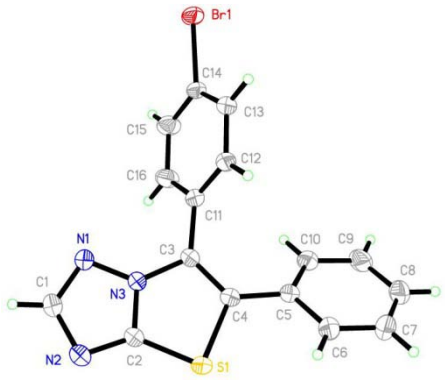
7. X-ray Structure, Crystallographic Data of 3ba and 3db



X-ray Structure of **3ba** (CCDC 894296)

(1) Selected bond distances (Å) and angles (°): Br(1)-C(14) 1.940(3), C(1)-N(1) 1.326(4), C(1)-N(2) 1.363(4), C(2)-N(2) 1.317(4), C(2)-N(3) 1.351(4), C(2)-S(1) 1.721(3), C(3)-C(4) 1.362(4), C(3)-N(3) 1.399(4), C(3)-C(11) 1.485(4), C(4)-C(5) 1.461(4), C(4)-S(1) 1.772(3), C(5)-C(10) 1.383(4), C(5)-C(6) 1.400(4), C(6)-C(7) 1.390(5), C(7)-C(8) 1.368(5), C(8)-C(9) 1.374(5), C(9)-C(10) 1.387(4), C(11)-C(12) 1.383(4), C(11)-C(16) 1.389(4), C(12)-C(13) 1.384(4), C(13)-C(14) 1.377(4), C(14)-C(15) 1.370(4), C(15)-C(16) 1.387(4), N(1)-N(3) 1.366(4), N(1)-C(1)-N(2) 117.5(3), N(2)-C(2)-N(3) 111.5(3), N(2)-C(2)-S(1) 138.1(3), N(3)-C(2)-S(1) 110.3(2), C(4)-C(3)-N(3) 110.0(3), C(4)-C(3)-C(11), 130.6(3), N(3)-C(3)-C(11) 119.3(3), C(3)-C(4)-C(5) 129.7(3), C(3)-C(4)-S(1) 112.2(2), C(5)-C(4)-S(1) 118.0(2), C(10)-C(5)-C(6) 118.3(3), C(10)-C(5)-C(4) 121.5(3), C(6)-C(5)-C(4) 120.1(3), C(7)-C(6)-C(5) 120.8(3), C(8)-C(7)-C(6) 120.2(4), C(7)-C(8)-C(9) 119.4(4), C(8)-C(9)-C(10) 121.3(3), C(5)-C(10)-C(9) 120.1(3), C(12)-C(11)-C(16) 119.6(3), C(12)-C(11)-C(3) 120.3(3), C(16)-C(11)-C(3) 119.9(3), C(11)-C(12)-C(13) 120.7(3), C(14)-C(13)-C(12) 118.3(3), C(15)-C(14)-C(13) 122.5(3), C(15)-C(14)-Br(1) 117.9(2), C(13)-C(14)-Br(1) 119.6(2), C(14)-C(15)-C(16) 118.8(3), C(15)-C(16)-C(11) 120.1(3), C(1)-N(1)-N(3) 100.3(3), C(2)-N(2)-C(1) 100.7(3), C(2)-N(3)-N(1) 109.9(2), C(2)-N(3)-C(3) 117.0(3), N(1)-N(3)-C(3) 133.1(3), C(2)-S(1)-C(4) 90.45(15).

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(2) Summary of crystallographic data for **3ba**

Compound	**3ba**
Molecular formula	$C_{16}H_{10}BrN_3S$
Molecular weight	356.24
Temperatur of collection (K)	296 (2)
Crystal system	Monoclinic
Space group	P2(1)/c
a (Å)	6.3583(10)
b (Å)	11.9472(18)
c (Å)	19.211(3)
α (^{o})	90.00
β (^{o})	91.318(2)
γ (^{o})	90.00
V, (Å^{-3})	1458.9(4)
Z	4
$D_{calc.}$ (g cm^{-3})	1.622
μ (mm^{-1})	2.956
F (000)	712
Crystal dimensions, mm	0.25 0.20 0.18
Theta range for data collection, (^{o})	2.01-26.00
Index range (*h*, *k*, *l*)	-7 to 7; -14 to 13; -22 to 22
No. of reflections measured	10605
No. of unique data	2803
No. of observed data [I>2 (I)]	2803
Absorption correction	none
Min. transmission	0.5253
Max. transmission	0.6182
Refinement method	full-matrix-least-squares on F^2
No. refined parameters	190
R_{int}	0.0397
R indices [I>2(I)]	R^1 = 0.0357; wR^2 = 0.0857
R indices (all data)	R^1 = 0.0539; wR^2 = 0.0917
Goodness of fit	1.032
Largest differenz peak and hole, (eÅ^{-3})	0.646 / -0.331

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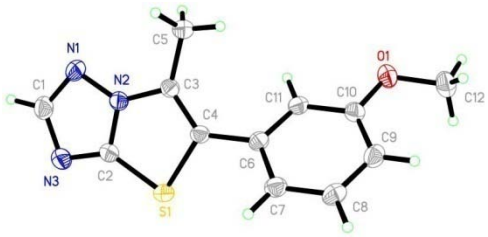

X-ray Structure of 3db (CCDC: 892215)

(1) Selected bond distances (Å) and angles (^{o}): C(1)-N(1) 1.324(3), C(1)-N(3) 1.364(3), C(2)-N(3) 1.330(3), C(2)-N(2) 1.344(2), C(2)-S(1) 1.7250(19), C(3)-C(4) 1.346(2), C(3)-N(2) 1.391(3), C(3)-C(5) 1.481(3), C(4)-C(6) 1.483(3), C(4)-S(1) 1.7736(19), C(6)-C(11) 1.384(3), C(6)-C(7) 1.397(3), C(7)-C(8) 1.376(3), C(8)-C(9) 1.381(3), C(9)-C(10) 1.392(3), C(10)-O(1) 1.366(2), C(10)-C(11) 1.387(3), C(12)-O(1) 1.424(3), N(1)-N(2) 1.362(2), N(1)-C(1)-N(3) 117.61(19), N(3)-C(2)-N(2) 111.48(17), N(3)-C(2)-S(1) 137.93(17), N(2)-C(2)-S(1) 110.59(14), C(4)-C(3)-N(2), 110.10(17), C(4)-C(3)-C(5) 130.90(19), N(2)-C(3)-C(5) 118.96(16), C(3)-C(4)-C(6) 128.85(18), C(3)-C(4)-S(1) 112.79(15), C(6)-C(4)-S(1) 118.36(14), C(11)-C(6)-C(7) 119.33(19), C(11)-C(6)-C(4) 120.29(17), C(7)-C(6)-C(4) 120.34(18), C(8)-C(7)-C(6) 119.6(2), C(7)-C(8)-C(9) 121.3(2), C(8)-C(9)-C(10) 119.30(19), O(1)-C(10)-C(11) 115.18(19), O(1)-C(10)-C(9) 125.1(2), C(11)-C(10)-C(9) 119.7(2), C(6)-C(11)-C(10) 120.77(19), C(1)-N(1)-N(2) 100.55(17), C(2)-N(2)-N(1) 110.12(17), C(2)-N(2)-C(3) 116.99(16), N(1)-N(2)-C(3) 132.88(18), C(2)-N(3)-C(1) 100.23(18), C(10)-O(1)-C(12) 118.22(18), C(2)-S(1)-C(4) 89.53(10).

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(2) Summary of crystallographic data for **3db**

Compound	**3db**
Molecular formula	$C_{12}H_{11}N_3OS$
Molecular weight	245.30
Temperatur of collection (K)	296 (2)
Crystal system	Orthorhombic
Space group	P 2 (1) 2 (1) 2 (1)
a (Å)	7.0809 (7)
b (Å)	7.6178 (8)
c (Å)	21.146 (2)
α (^{o})	90.00
β (^{o})	90.00
γ (^{o})	90.00
V, (Å^{-3})	1140.6 (2)
Z	4
$D_{calc.}$ (g cm^{-3})	1.428
μ (mm^{-1})	0.269
F (000)	512
Crystal dimensions, mm	0.28 0.27 0.15
Theta range for data collection, (^{o})	1.93-25.98
Index range (*h*, *k*, *l*)	-8 to 7; -9 to 8; -25 to 25
No. of reflections measured	8475
No. of unique data	2189
No. of observed data [I>2 (I)]	4715
Absorption correction	none
Min. transmission	0.9284
Max. transmission	0.9607
Refinement method	full-matrix-least-squares on F^2
No. refined parameters	156
R_{int}	0.0456
R indices [I>2(I)]	R^1 = 0.0327; wR^2 = 0.0707
R indices (all data)	R^1 = 0.0456; wR^2 = 0.0754
Goodness of fit	1.040
Absolute structure parameter	-0.04 (8)
Largest differenz peak and hole, (eÅ^{-3})	0.119 / -0.201

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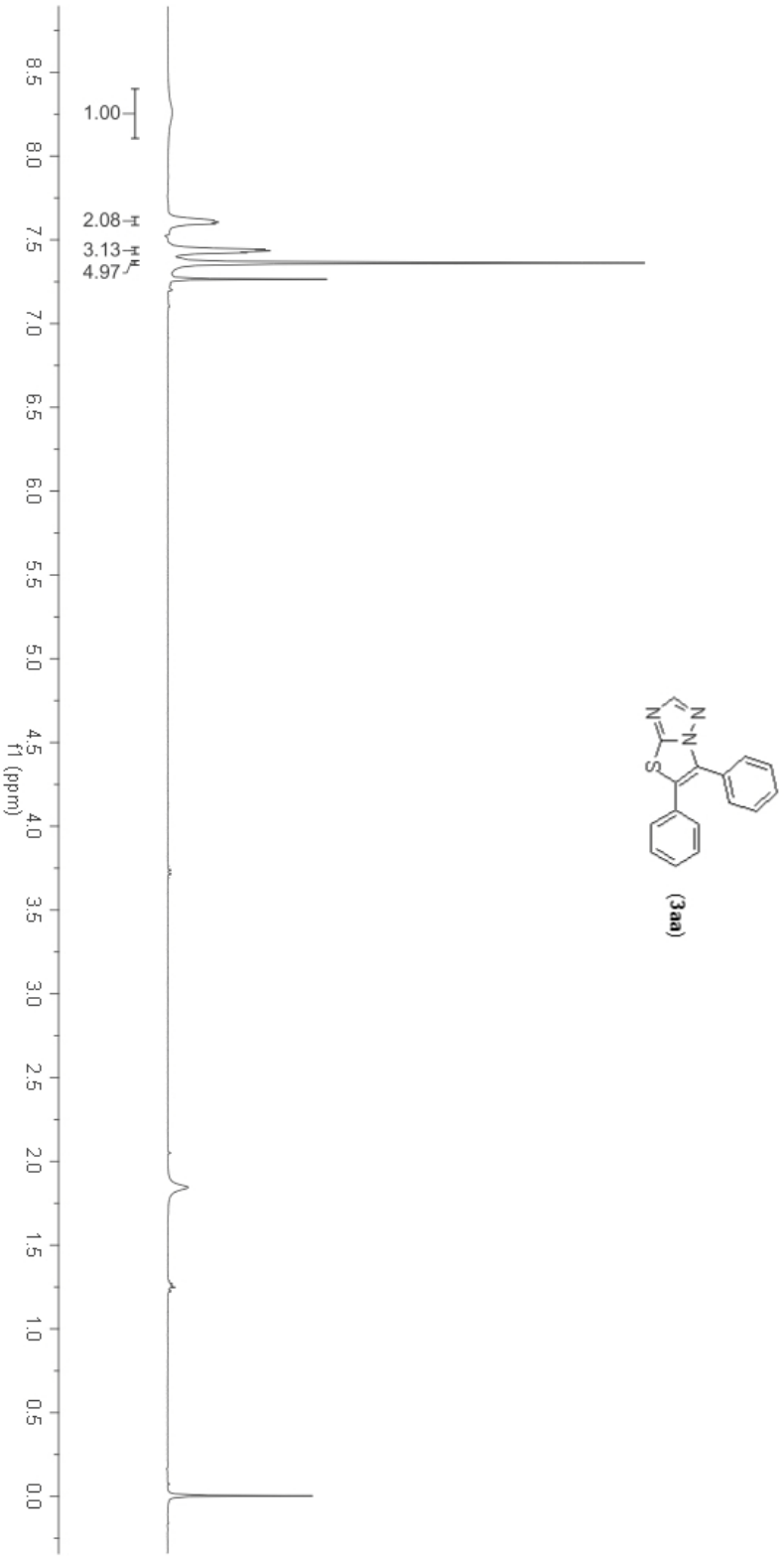
8. ^{1}H and ^{13}C NMR Spectra of Arylation Products

[^{1}H NMR Spectra of **3aa**]



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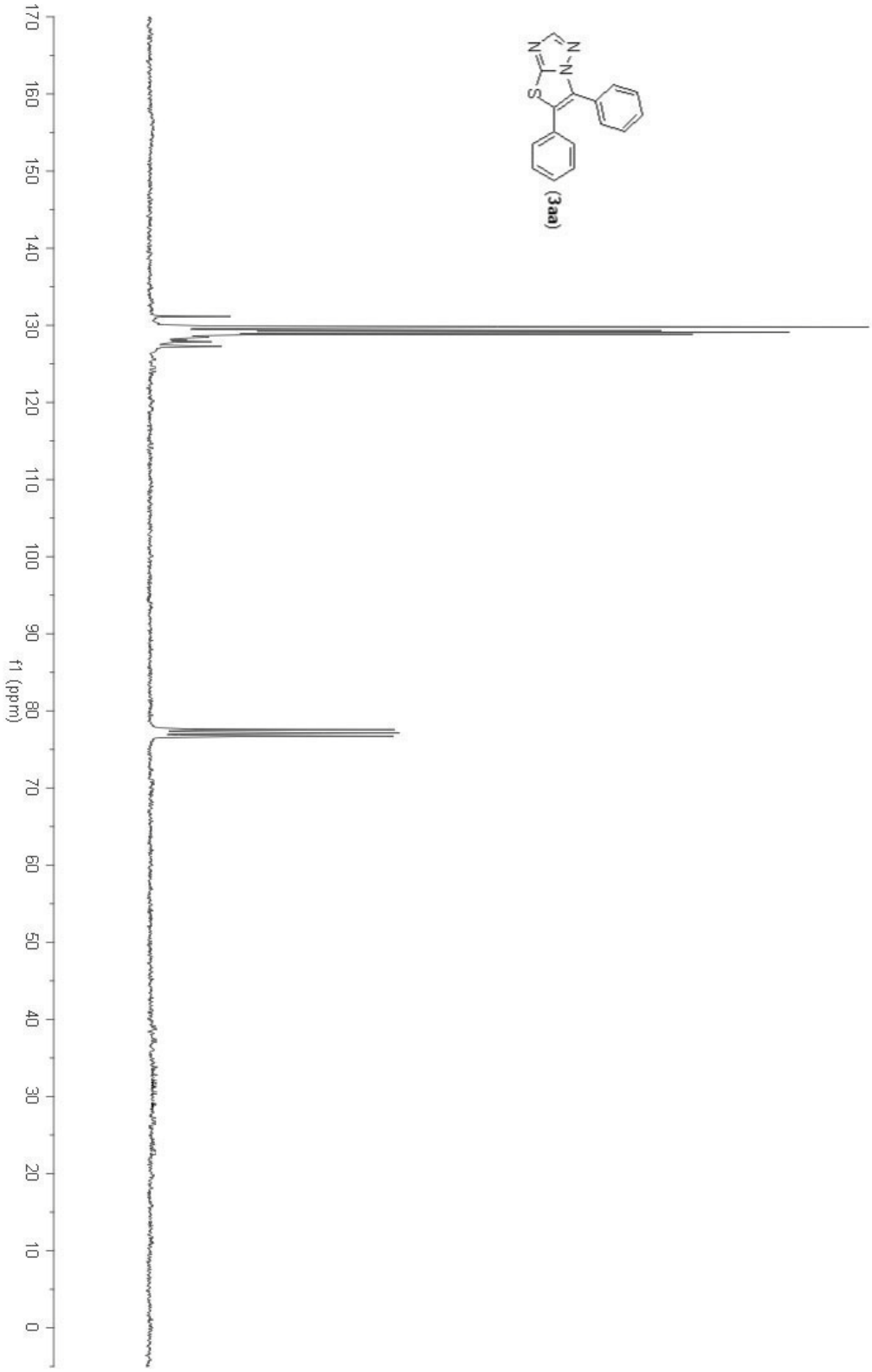
[^{13}C NMR Spectra of **3aa**]



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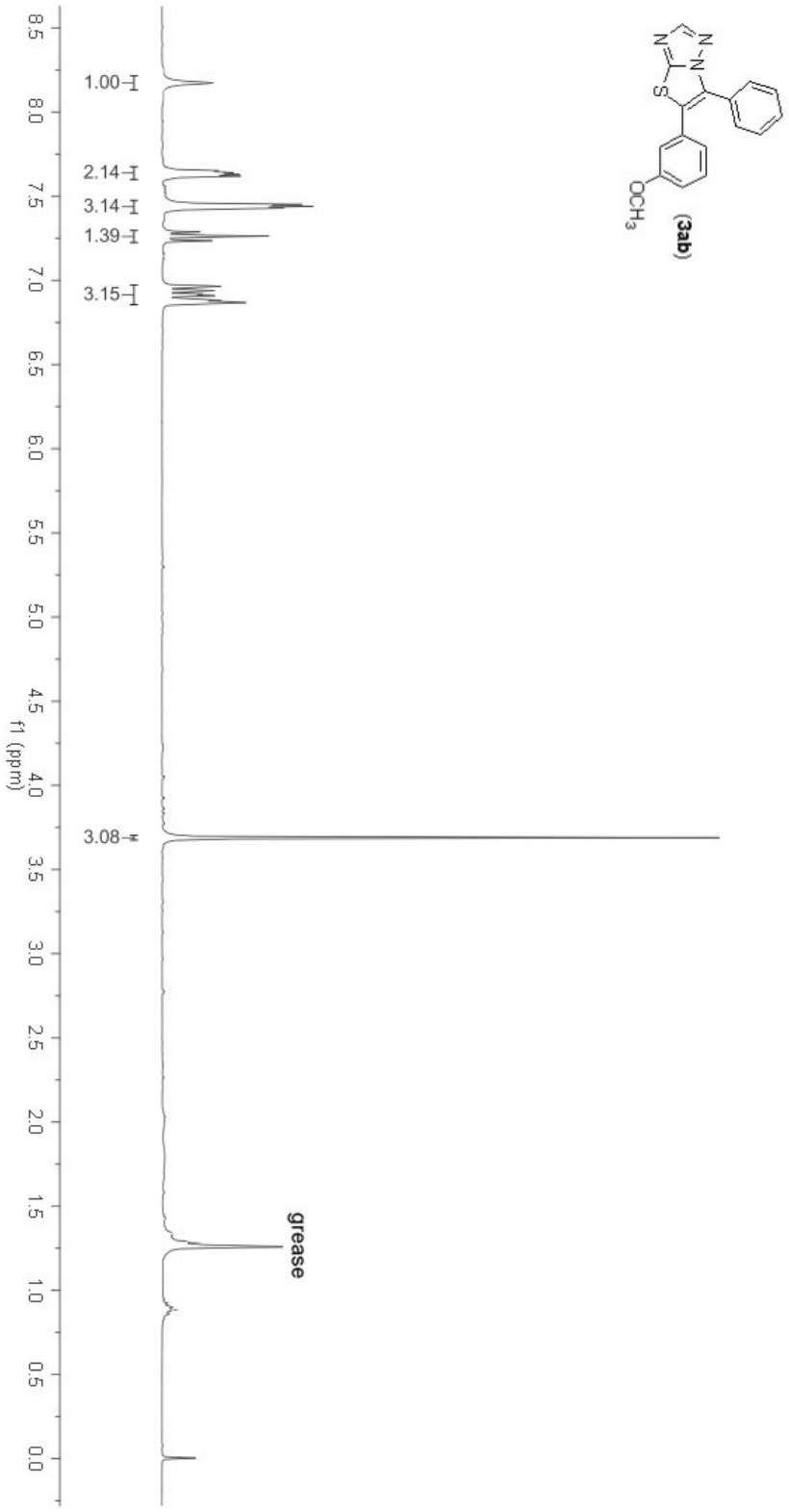
[^{1}H NMR Spectra of **3ab**]



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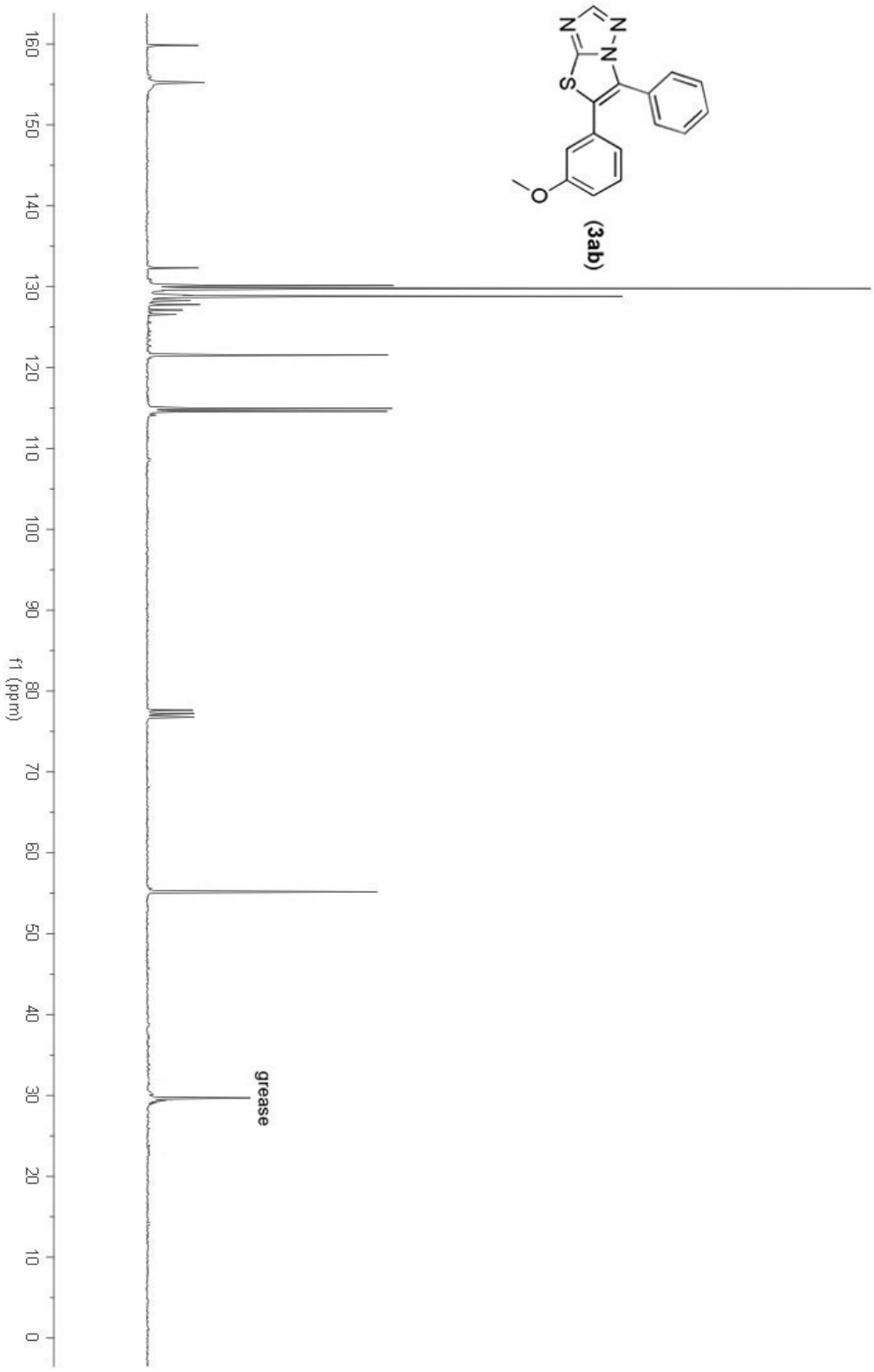
[^{13}C NMR Spectra of **3ab**]



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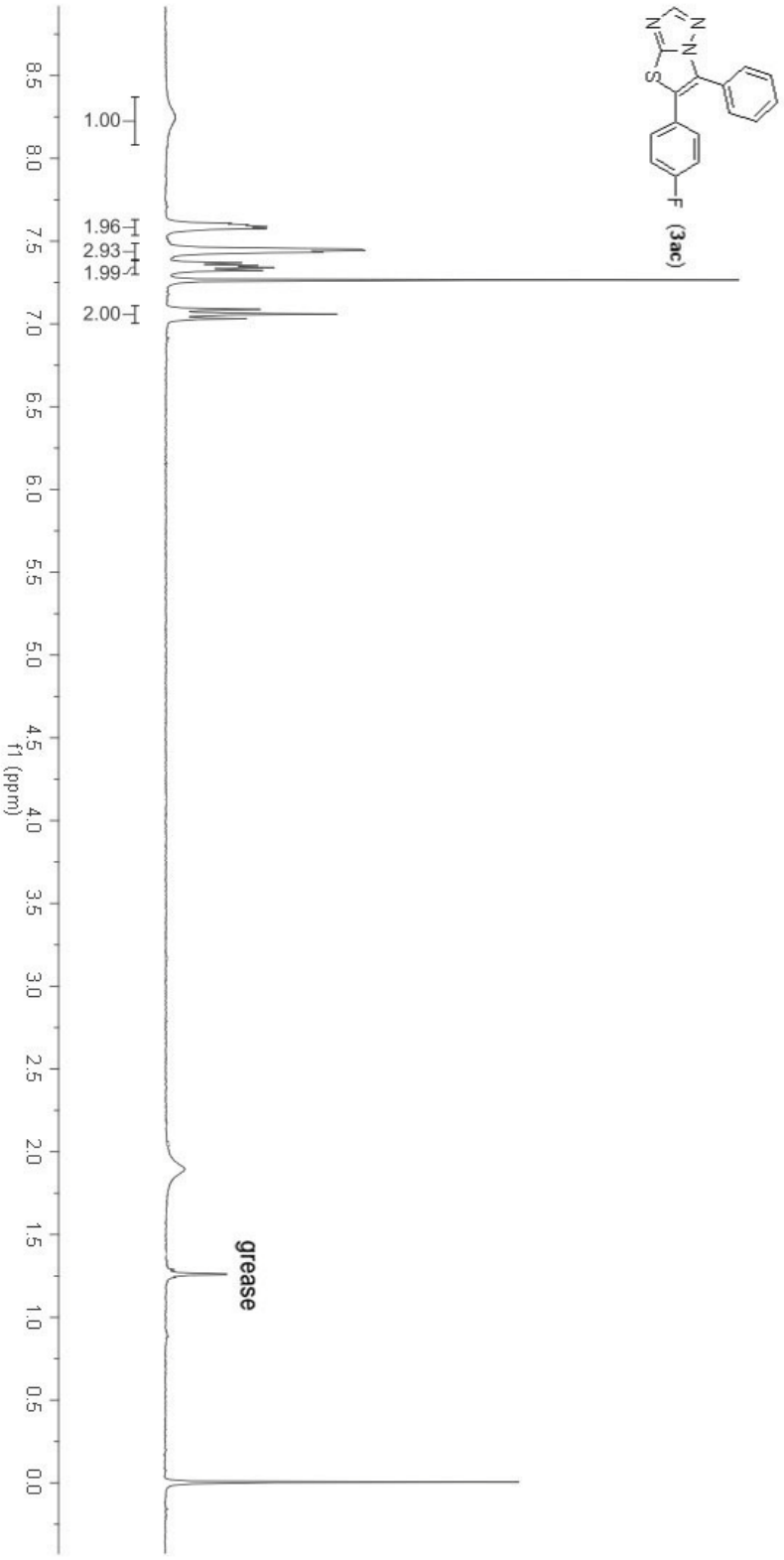
[^{1}H NMR Spectra of **3ac**]



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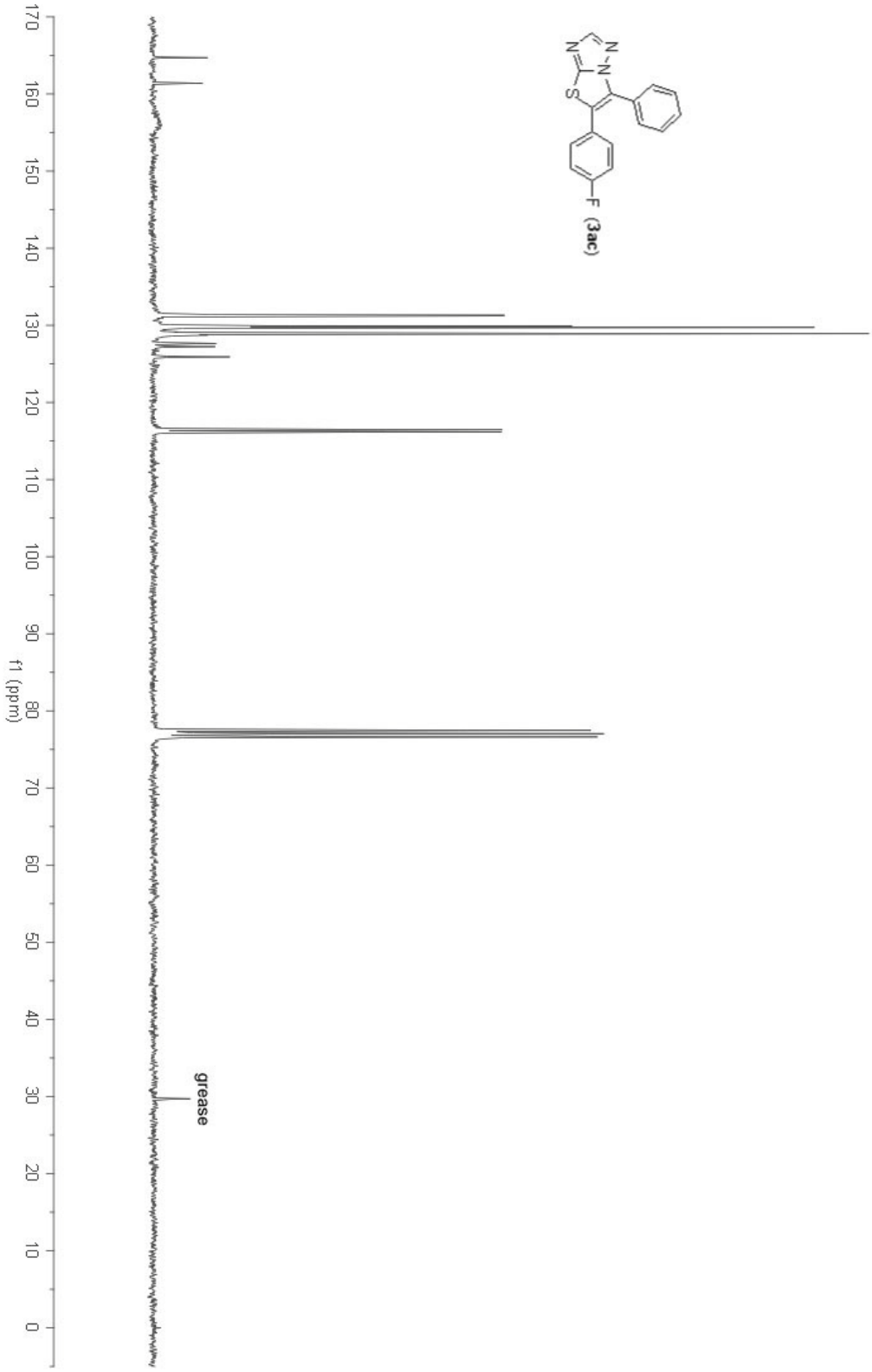
[^{13}C NMR Spectra of **3ac**]



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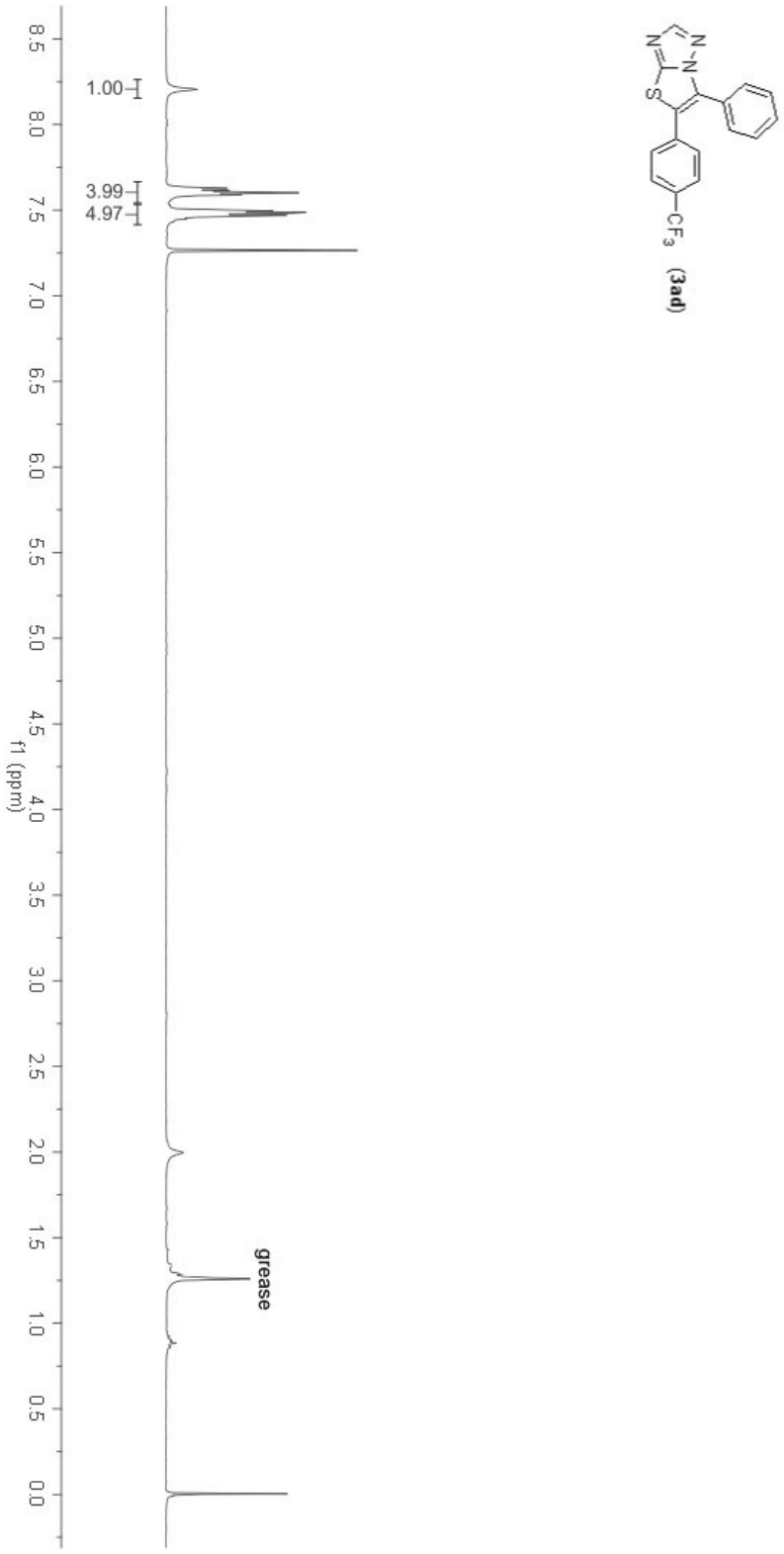
[^{1}H NMR Spectra of **3ad**]



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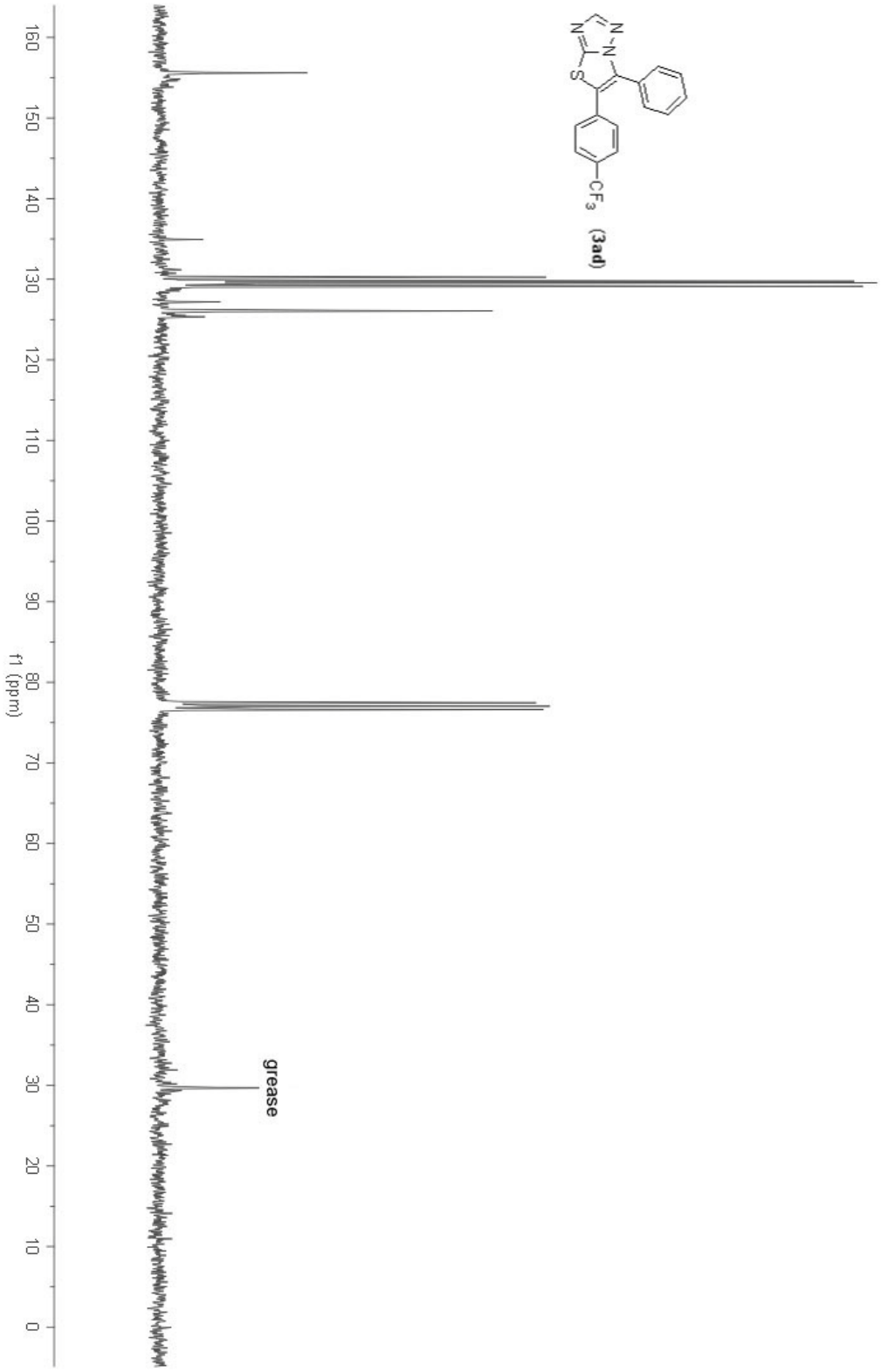
[^{13}C NMR Spectra of **3ad**]



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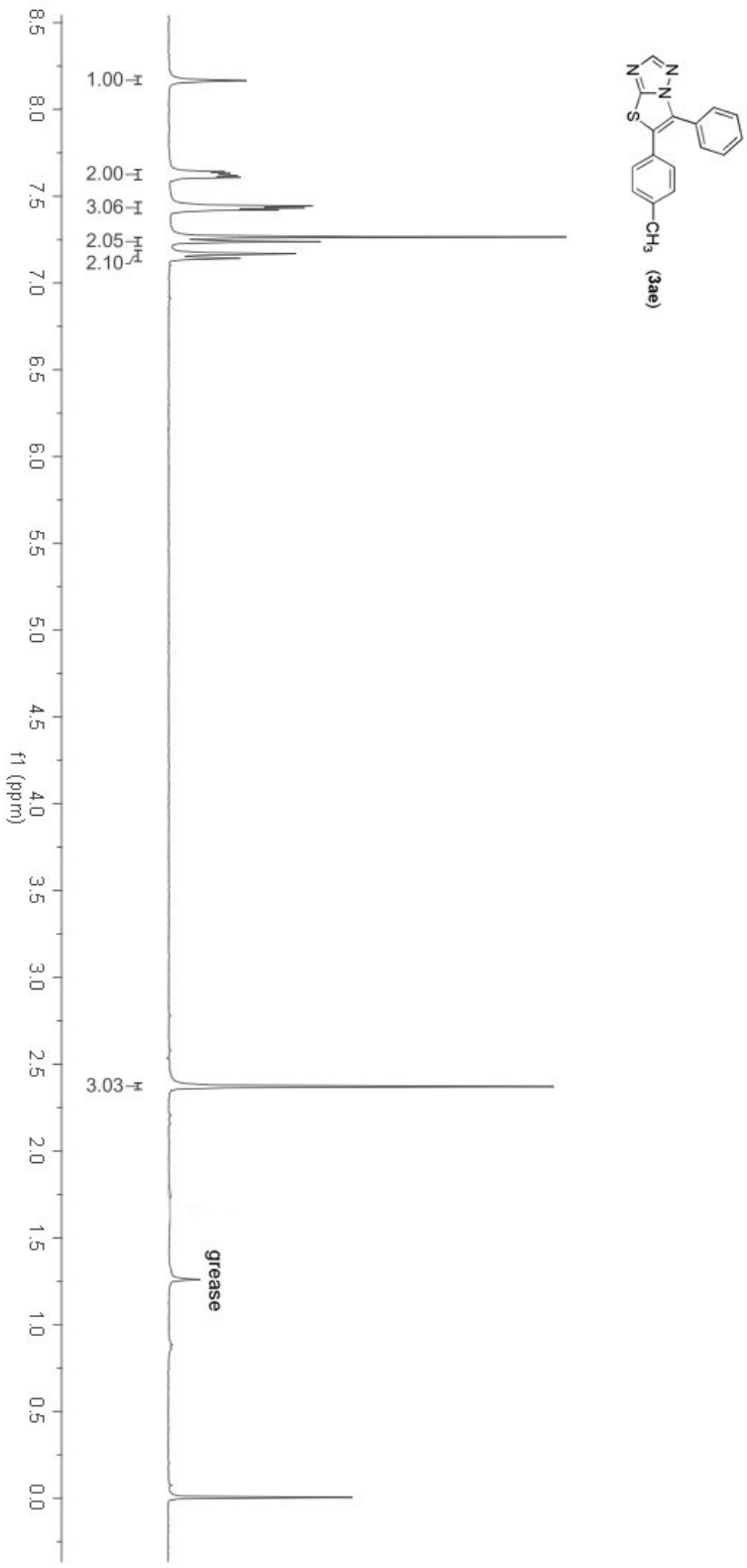
[^{1}H NMR Spectra of **3ae**]



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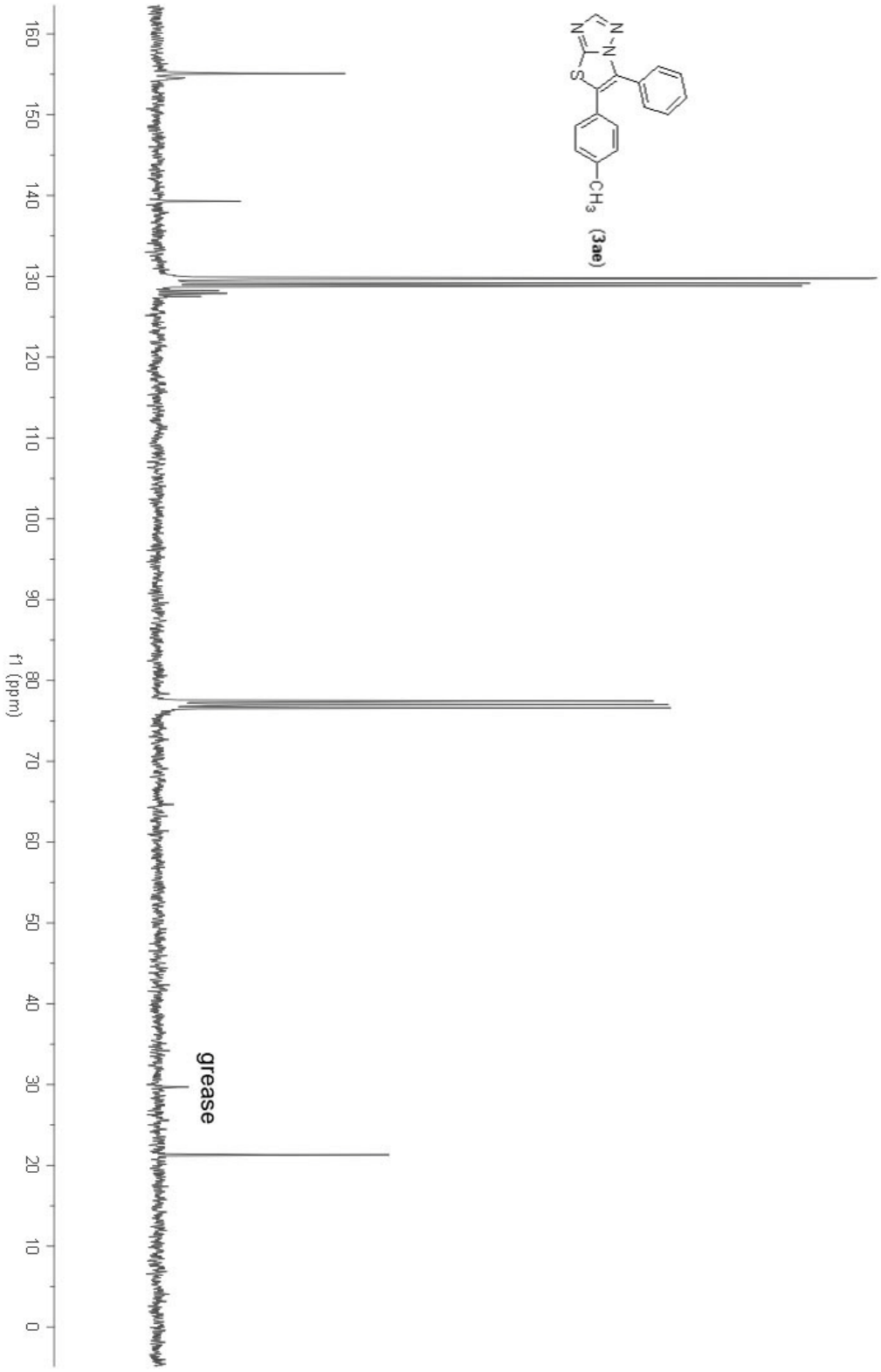
[^{13}C NMR Spectra of **3ae**]



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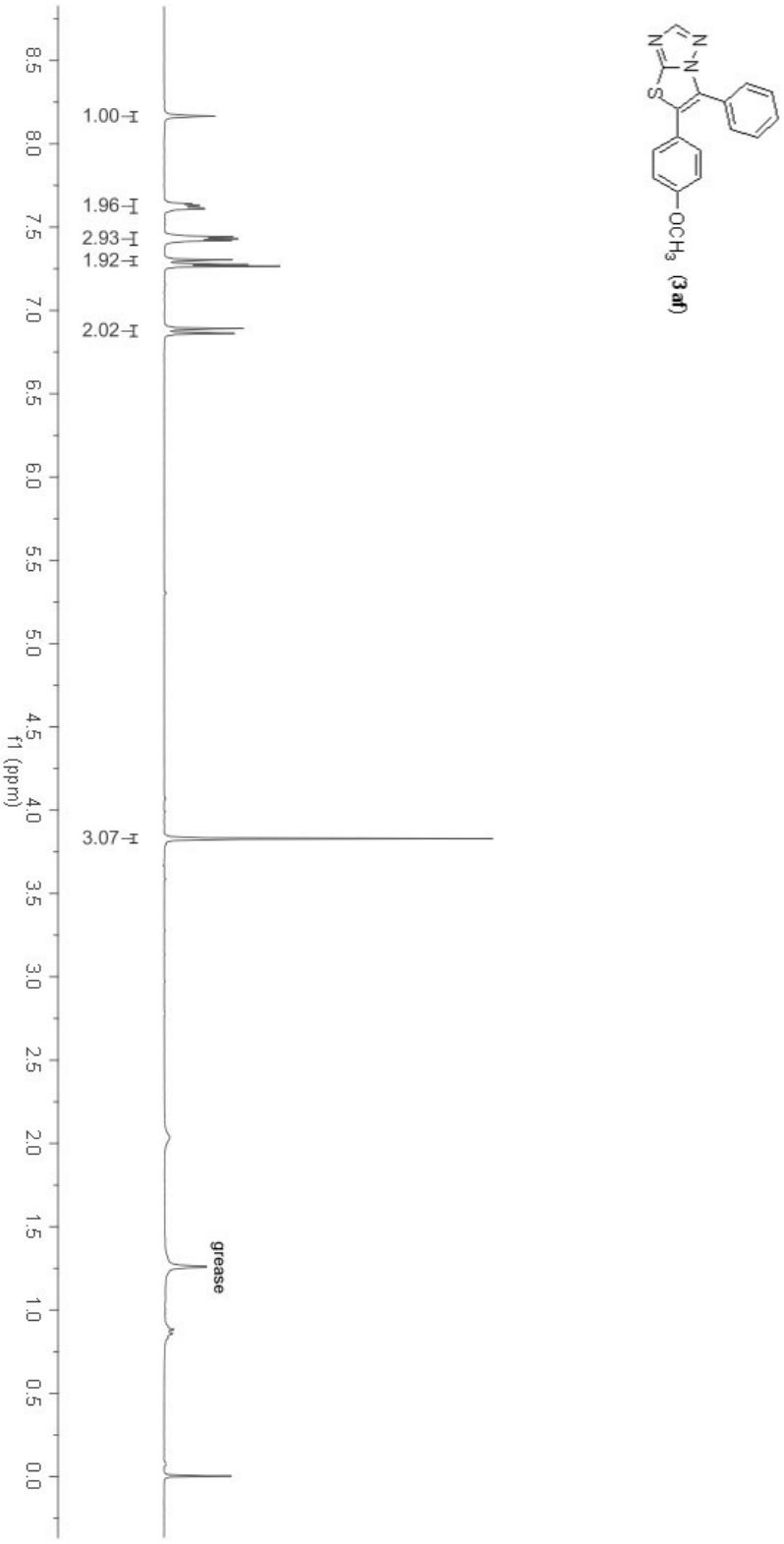
[^{1}H NMR Spectra of **3af**]



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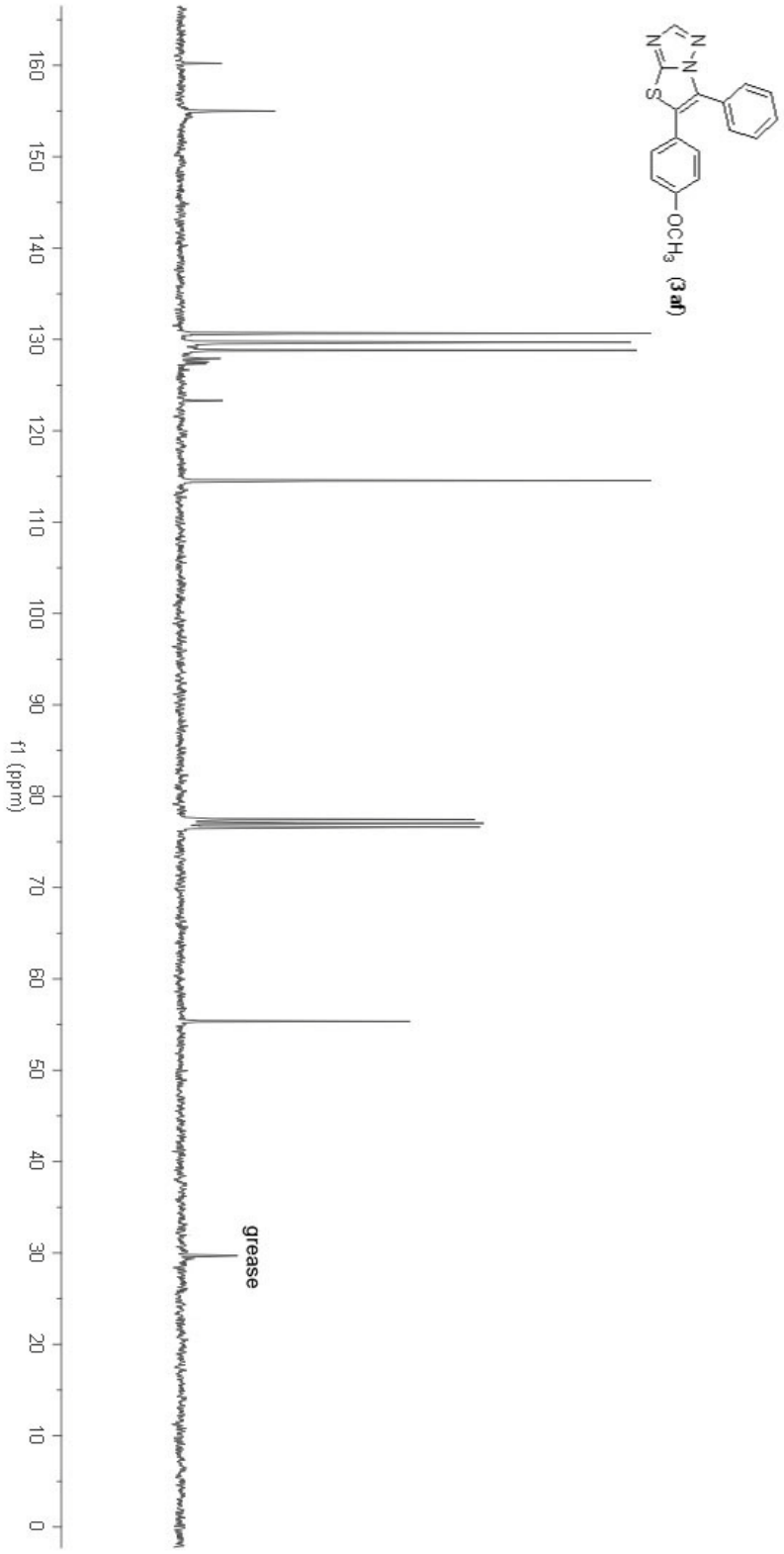
[^{13}C NMR Spectra of **3af**]



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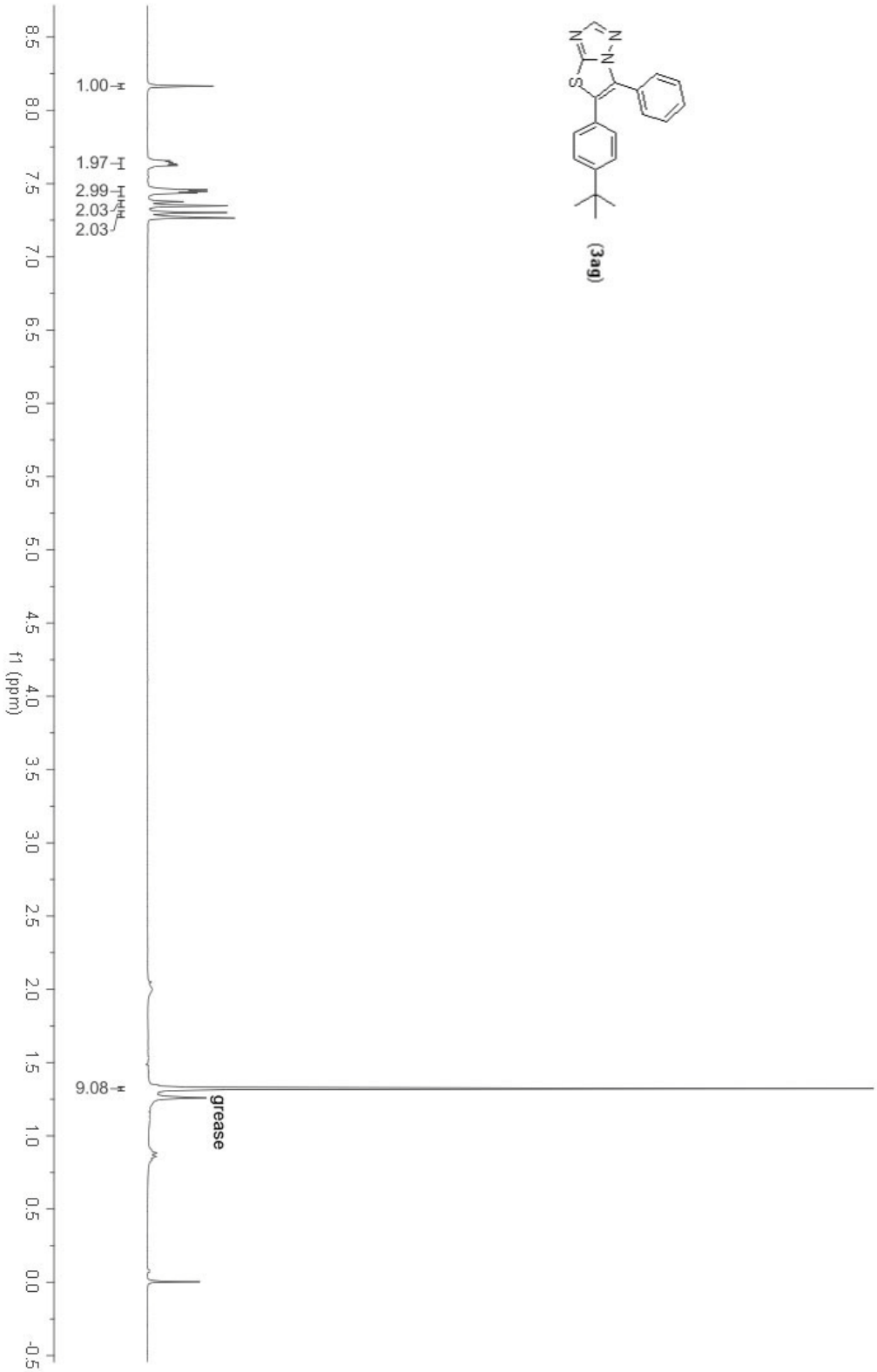
[^{1}H NMR Spectra of **3ag**]



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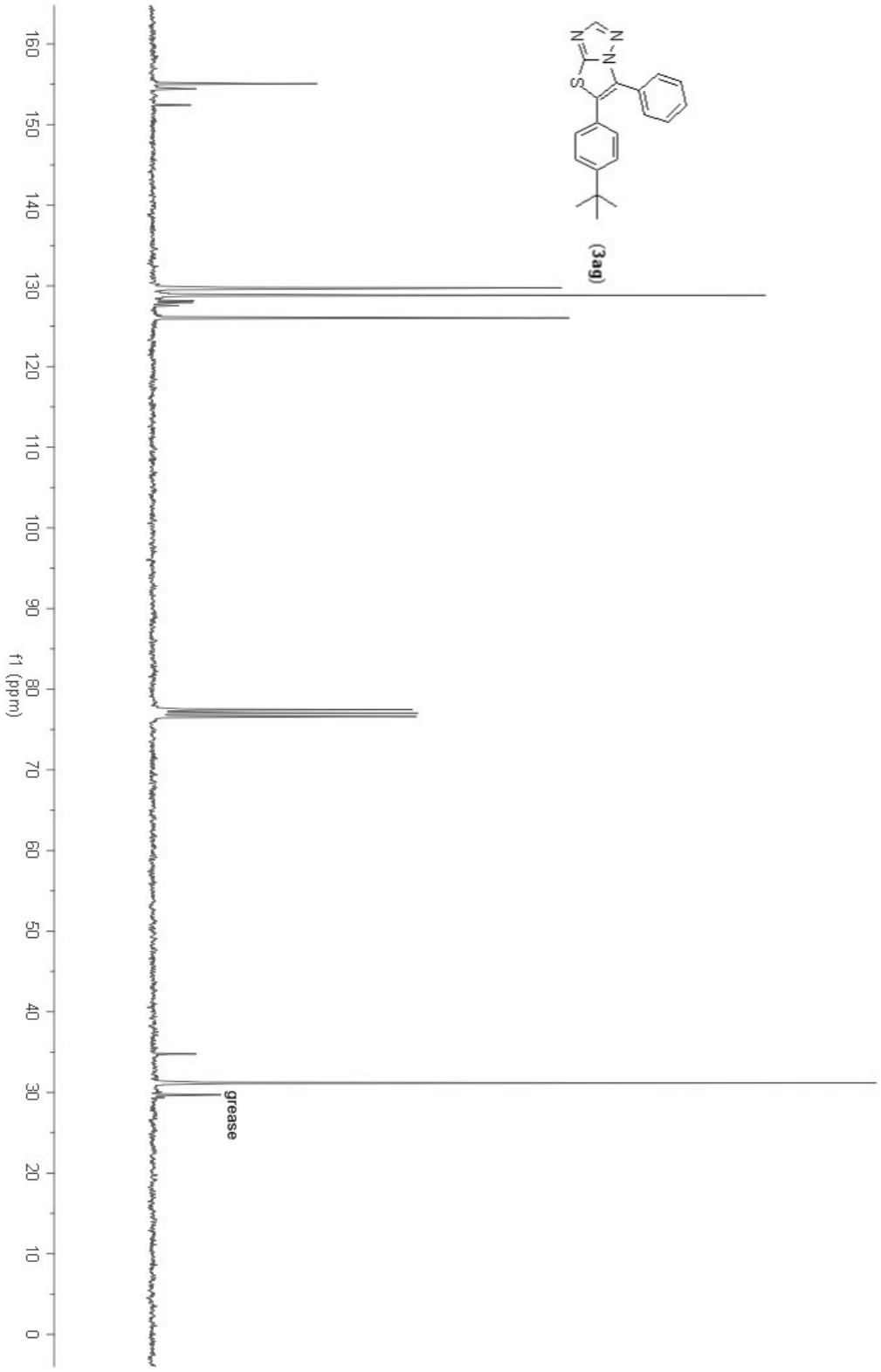
[^{13}C NMR Spectra of **3ag**]



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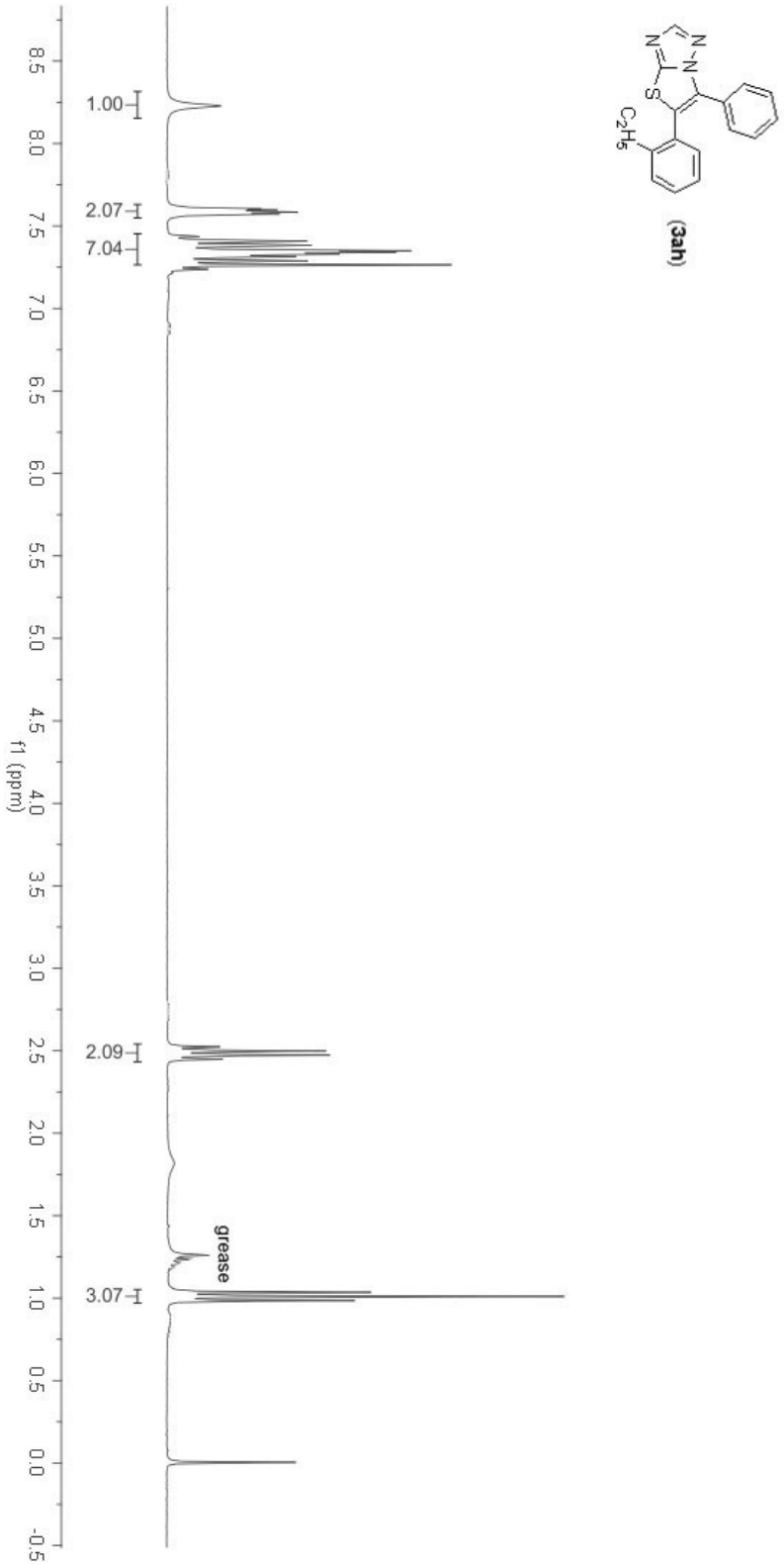
[^{1}H NMR Spectra of **3ah**]



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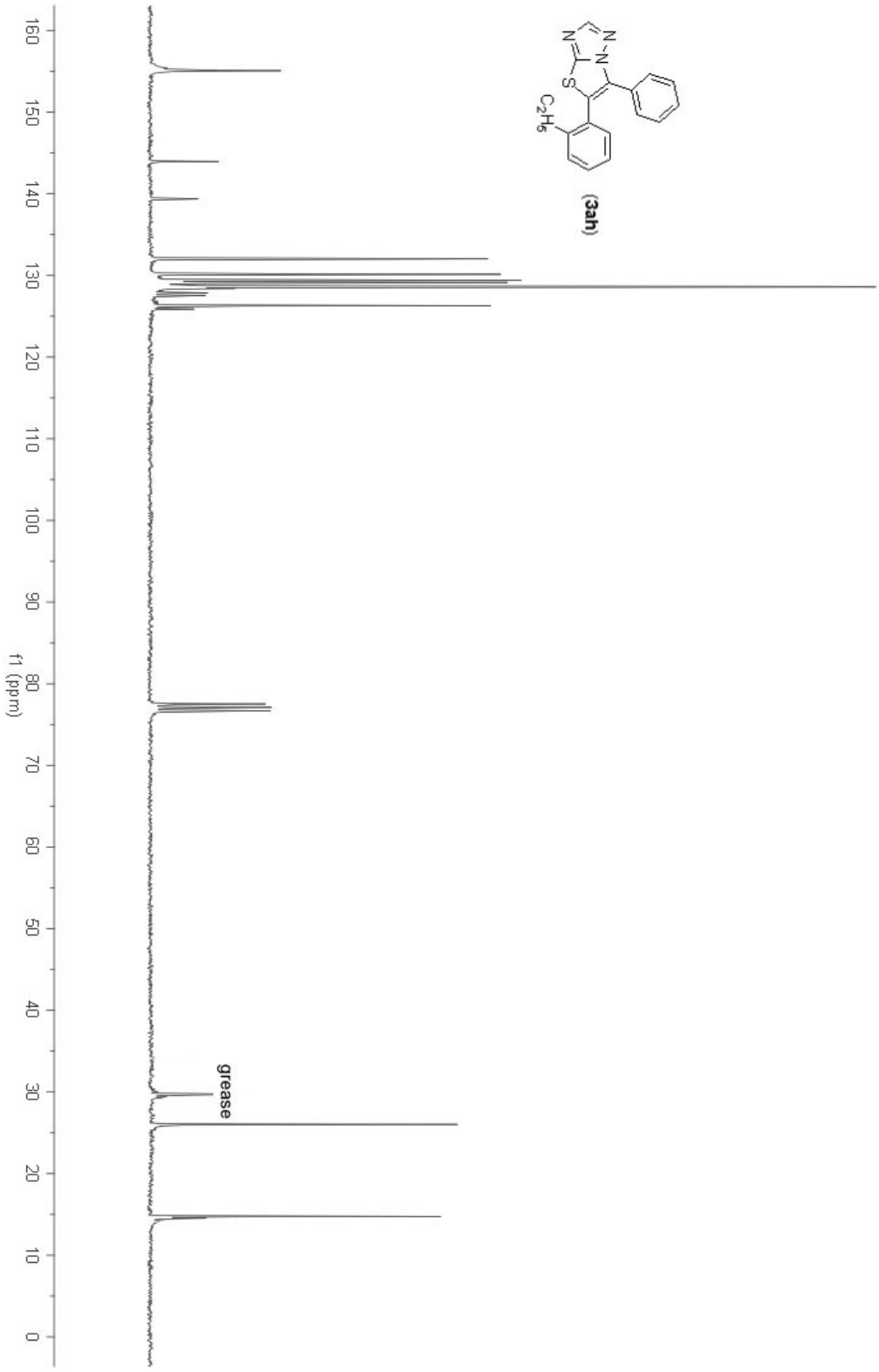
[^{13}C NMR Spectra of **3ah**]



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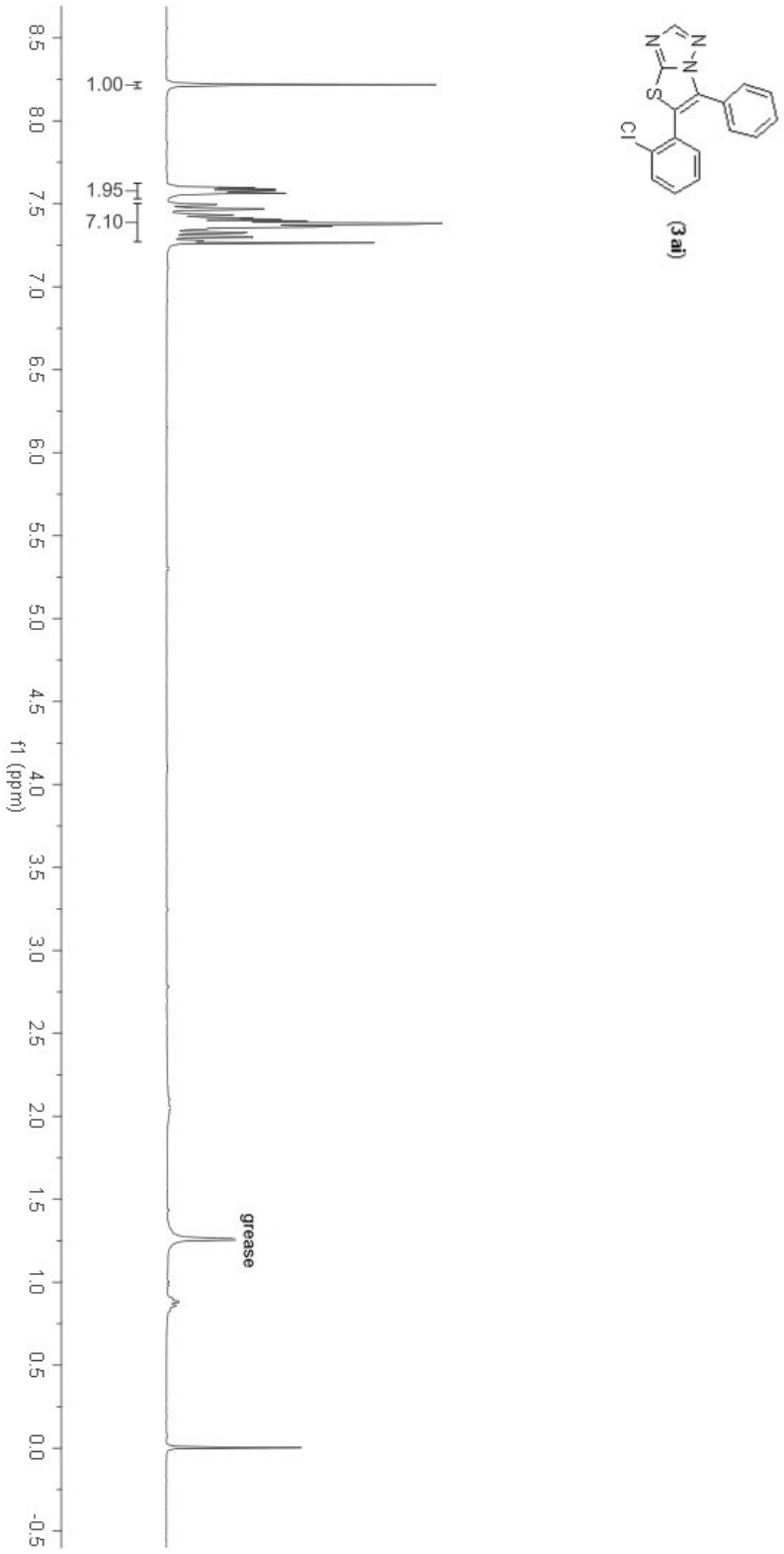
[^{1}H NMR Spectra of **3ai**]



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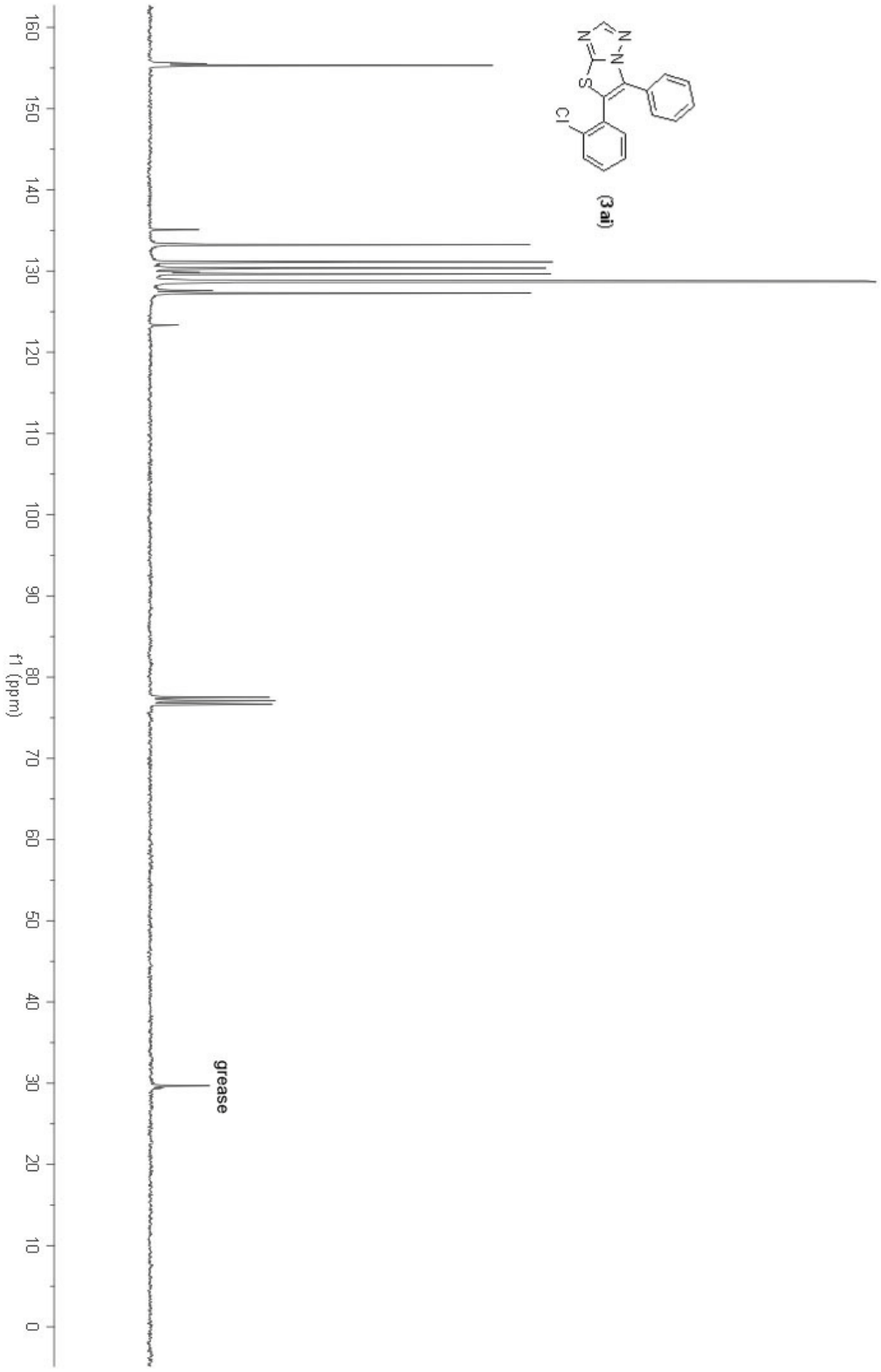

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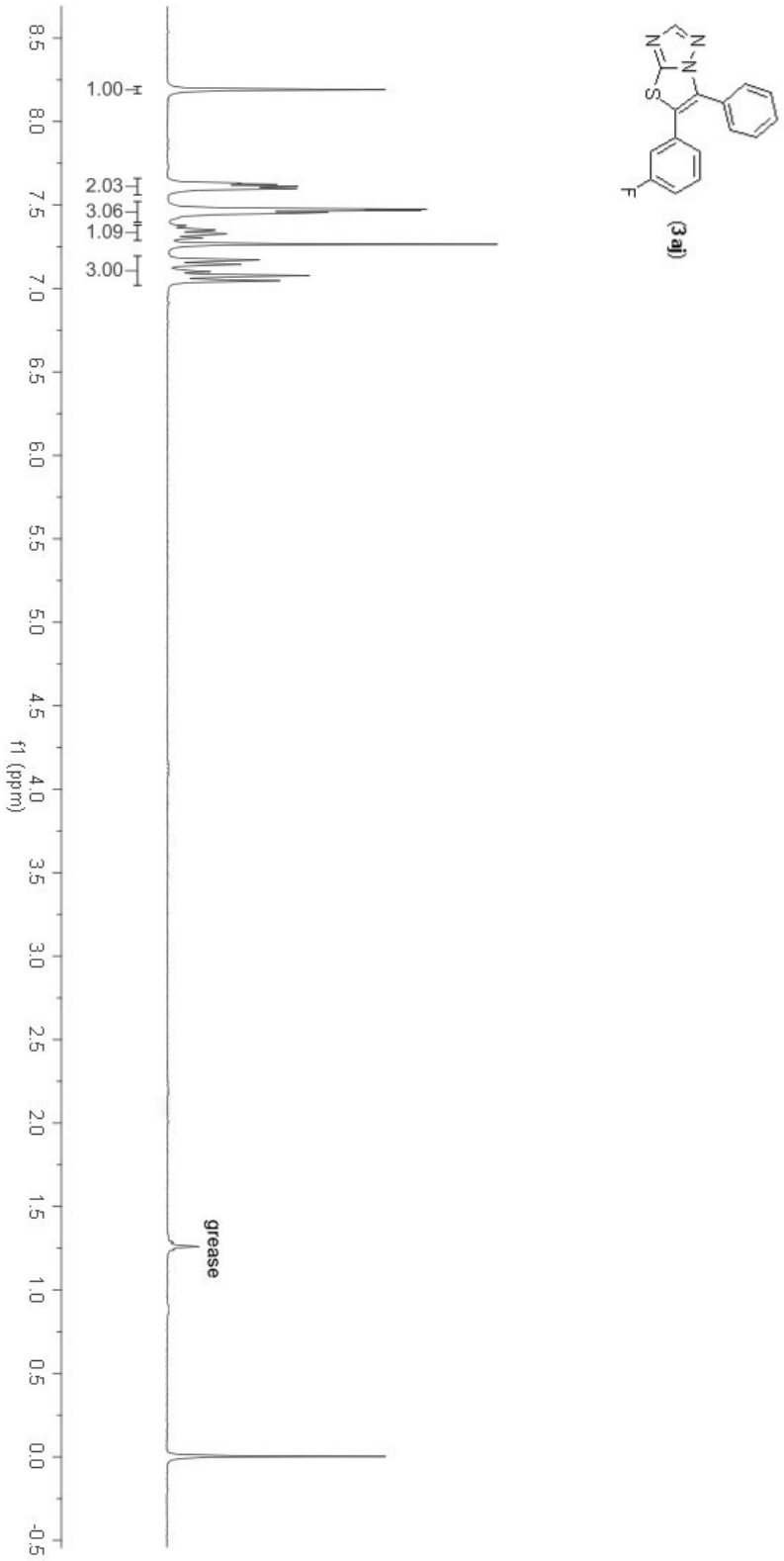

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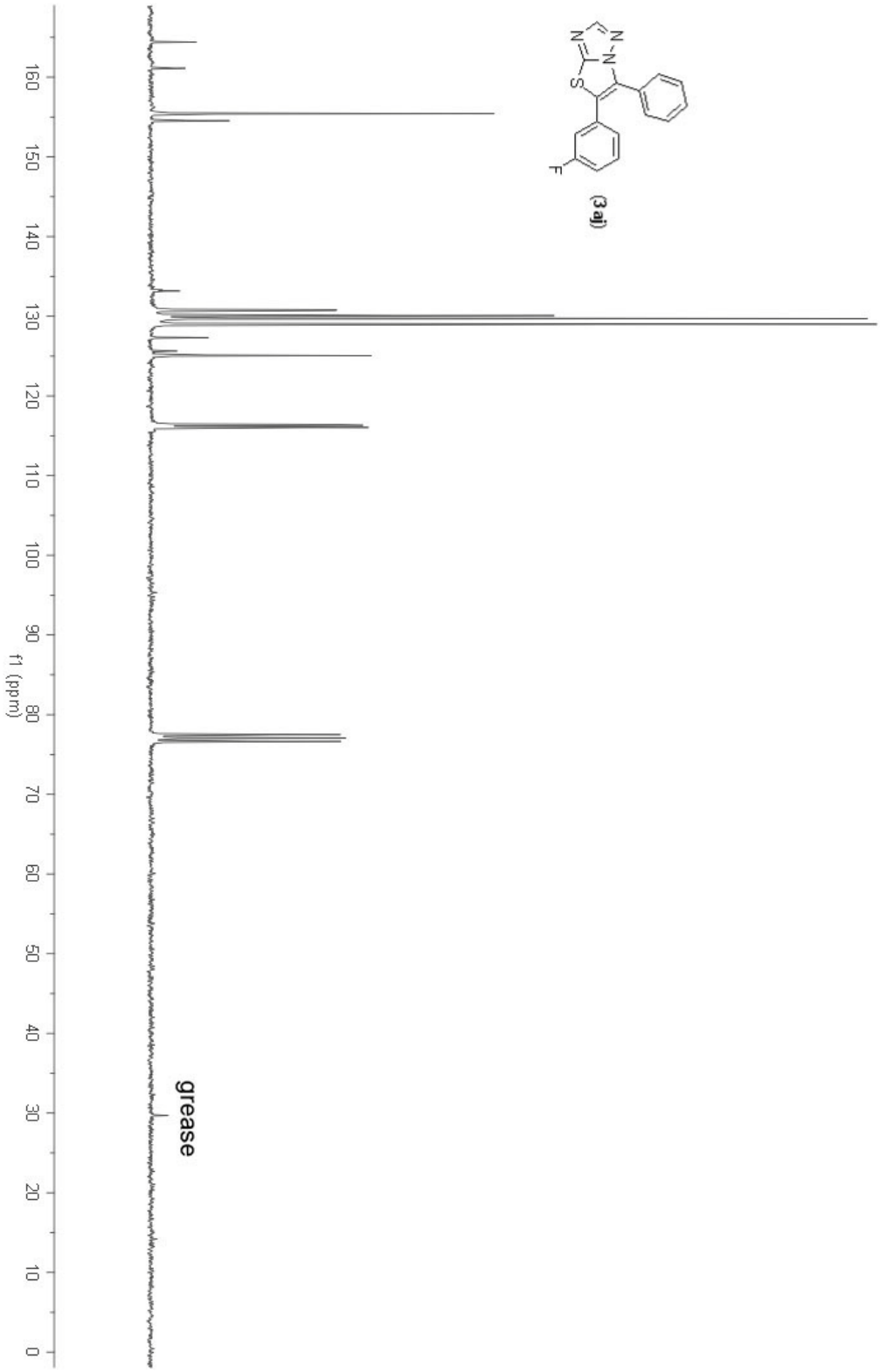

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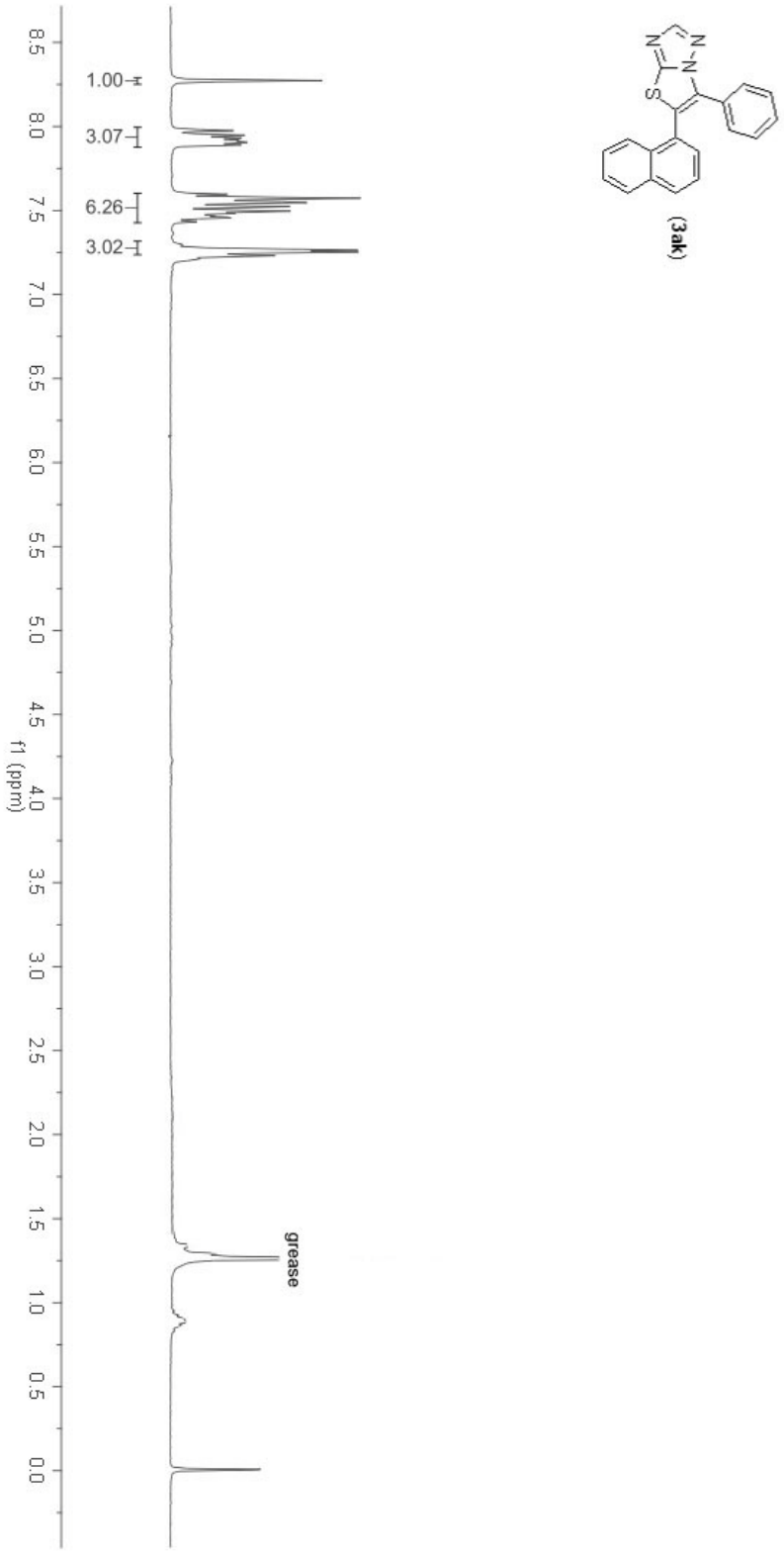
[^{1}H NMR Spectra of **3ak**]



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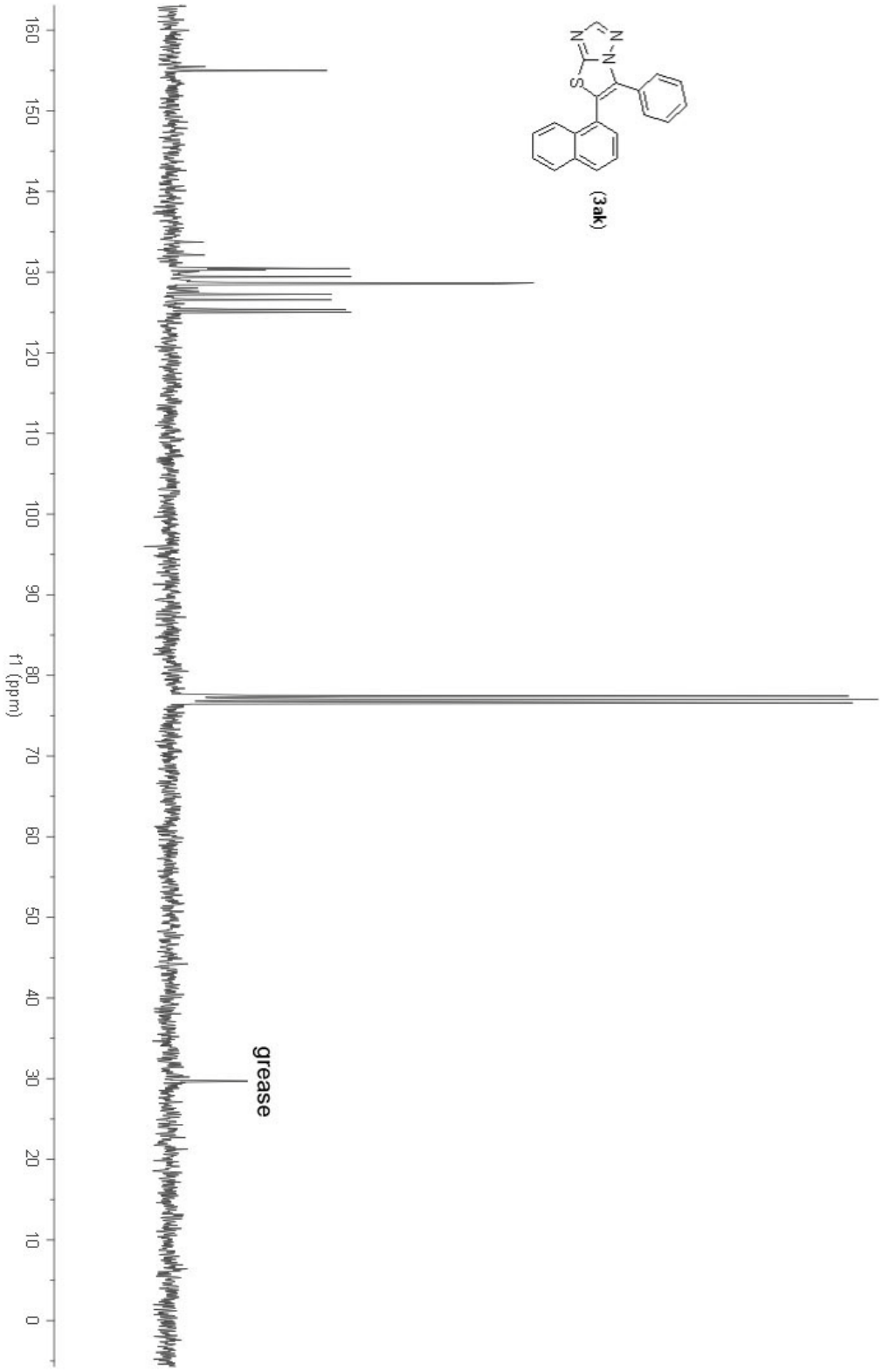

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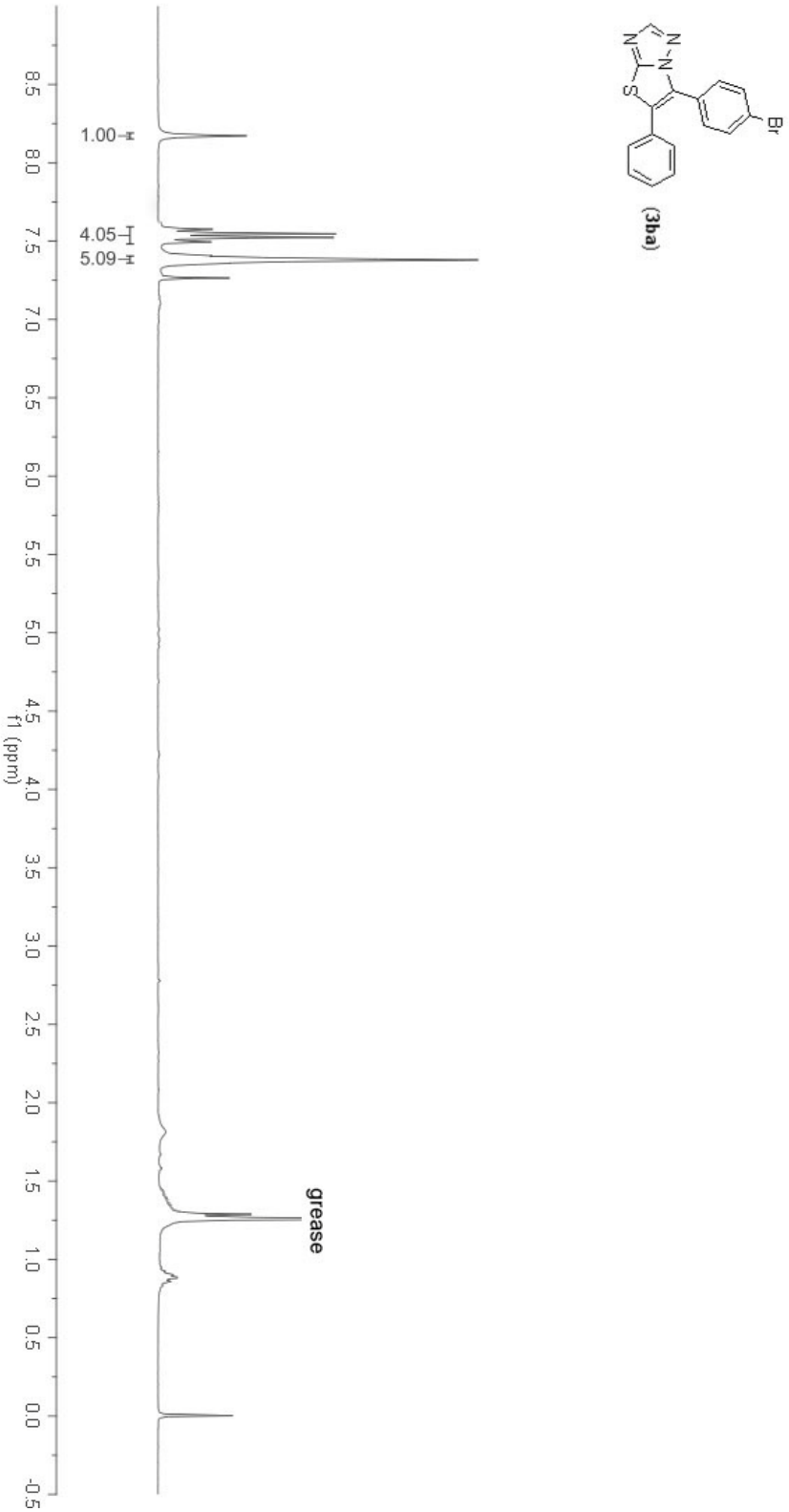
[^{1}H NMR Spectra of **3ba**]



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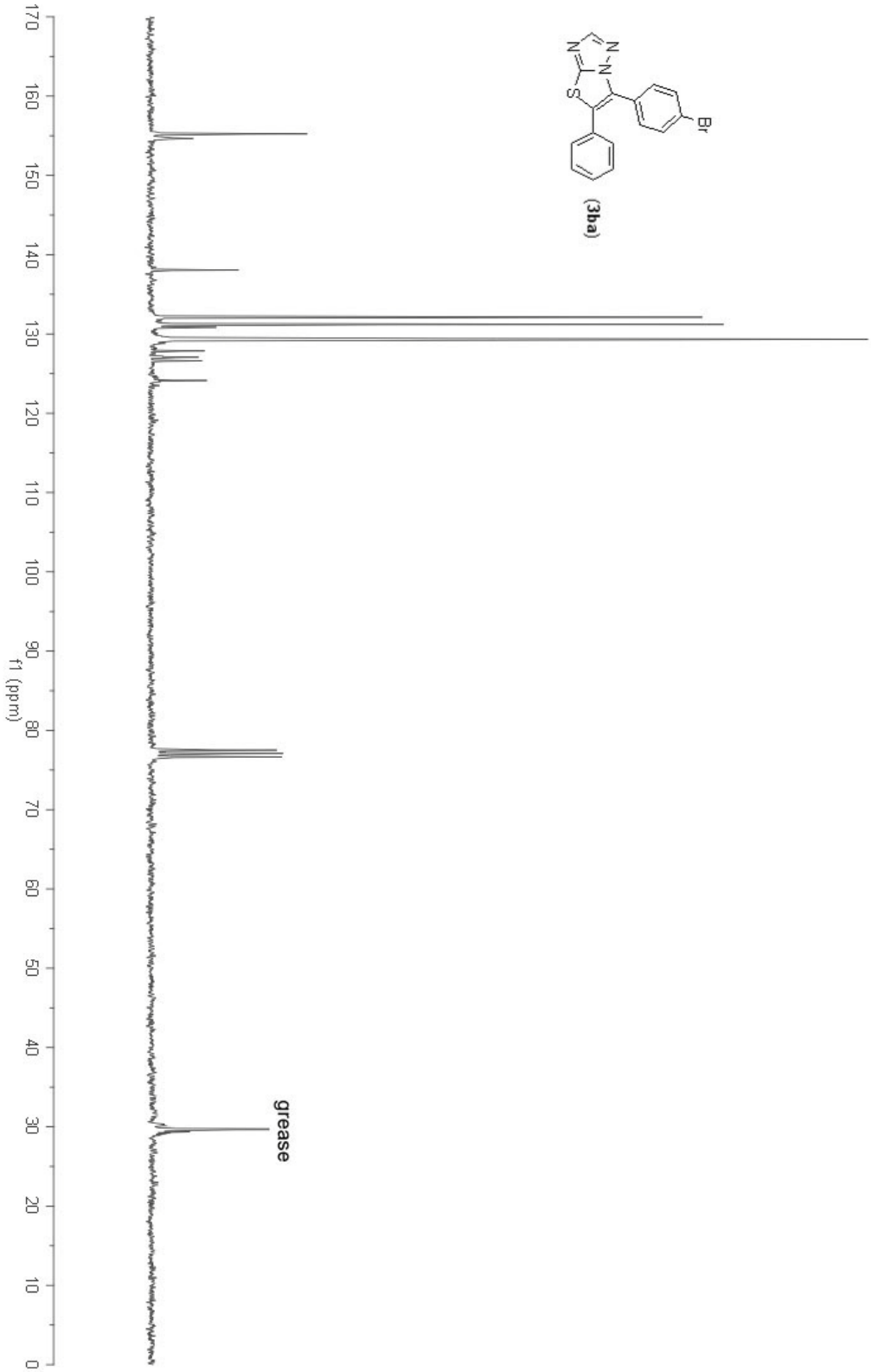

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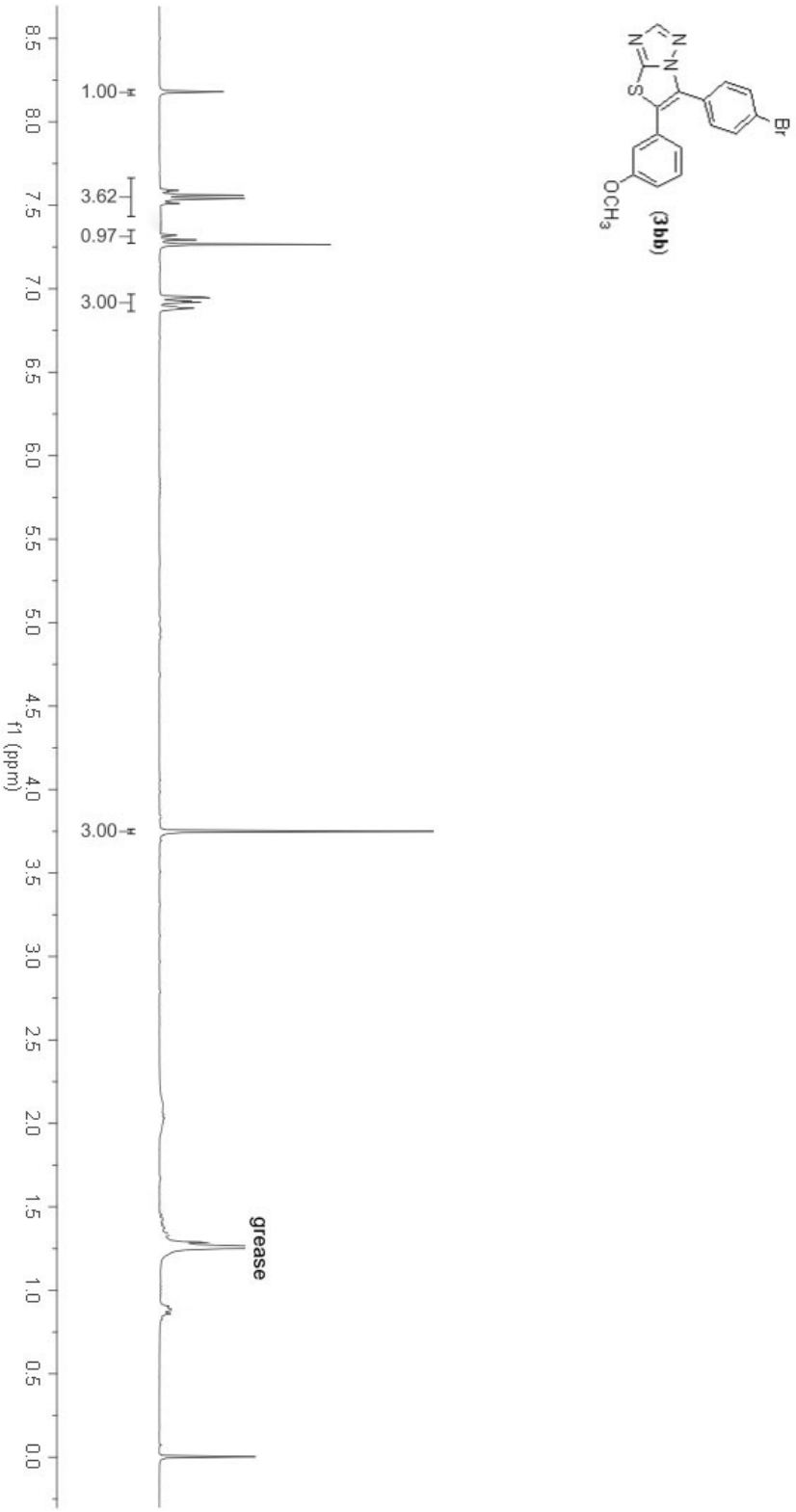

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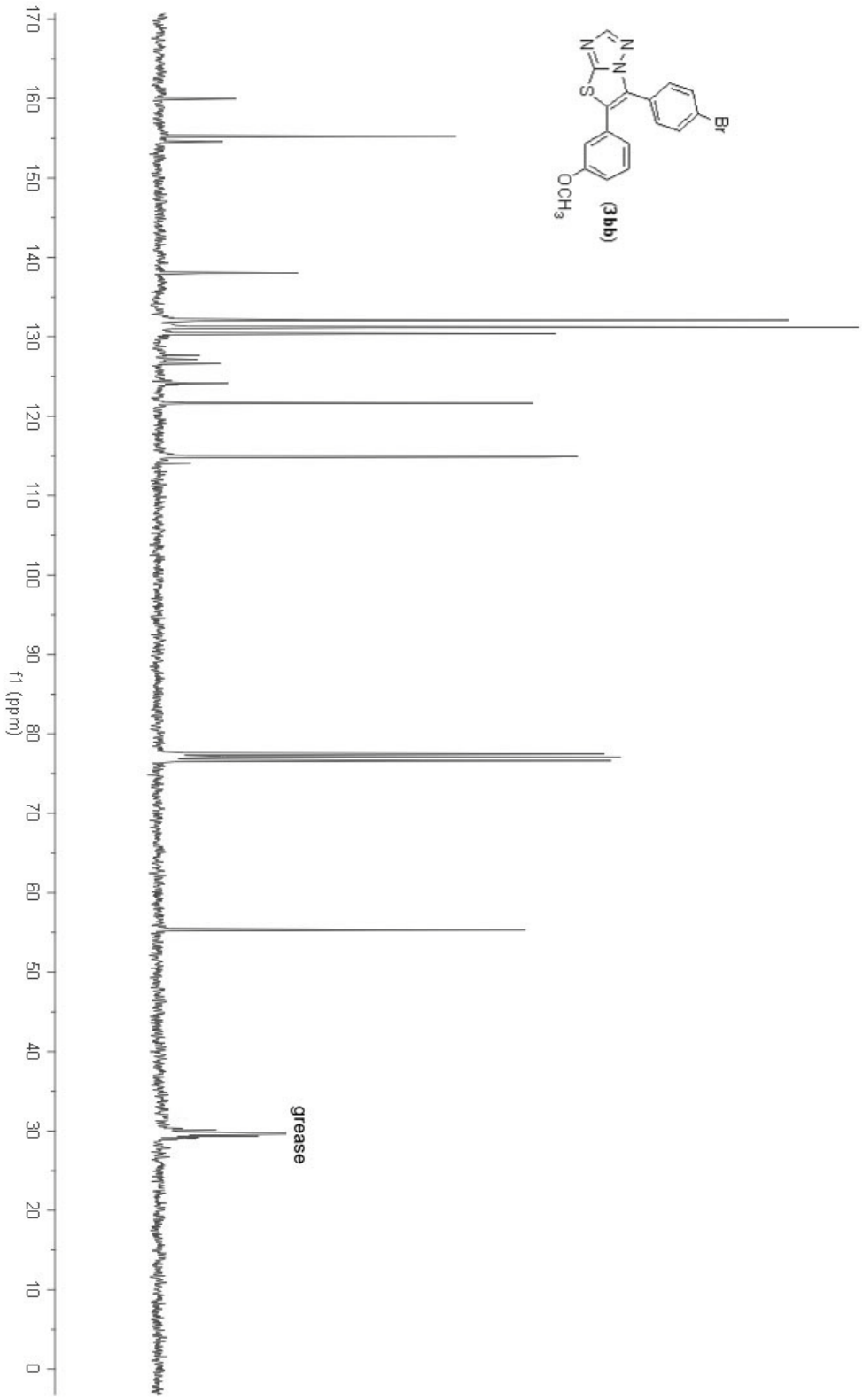

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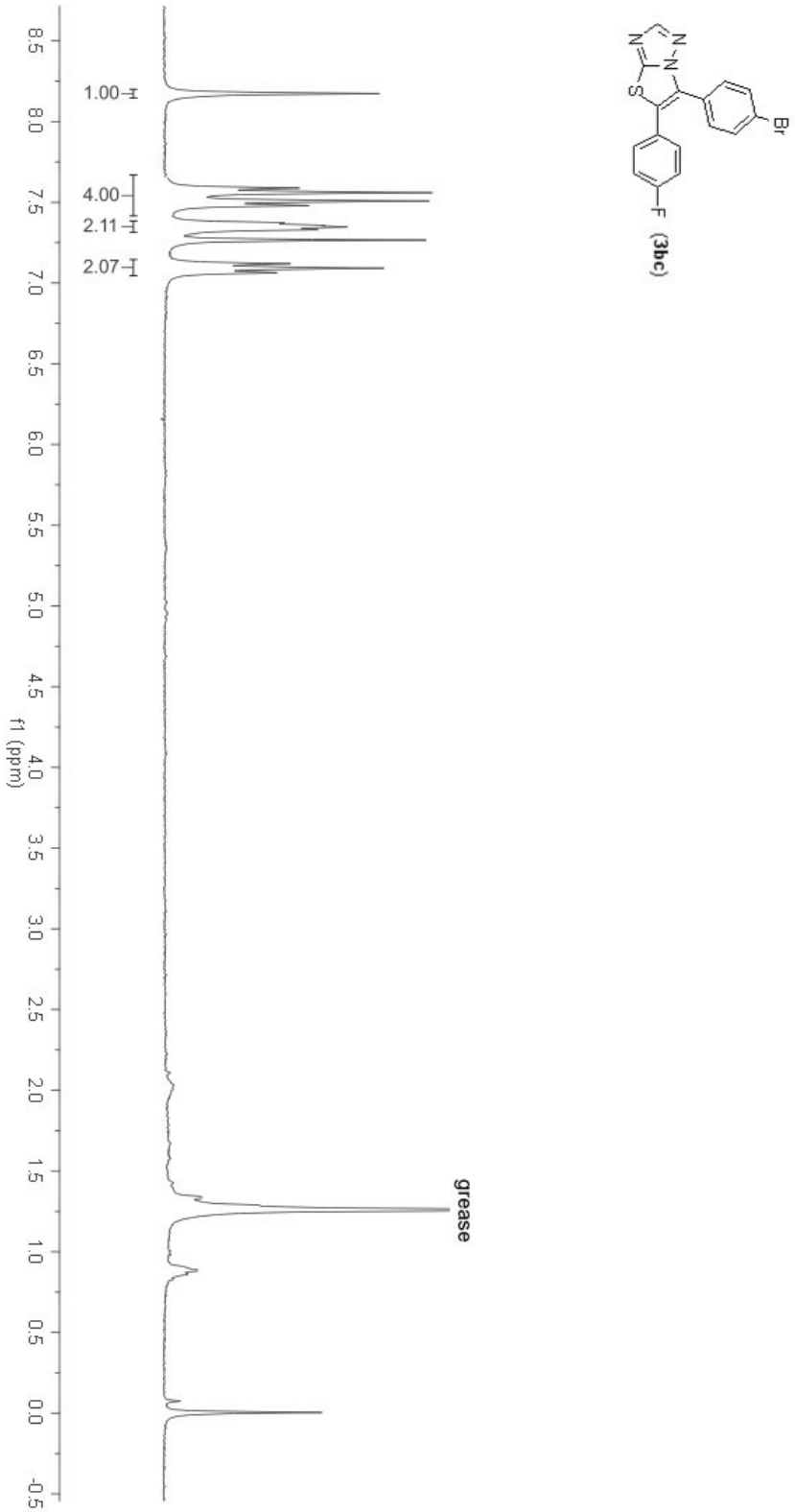
[^{1}H NMR Spectra of **3bc**]



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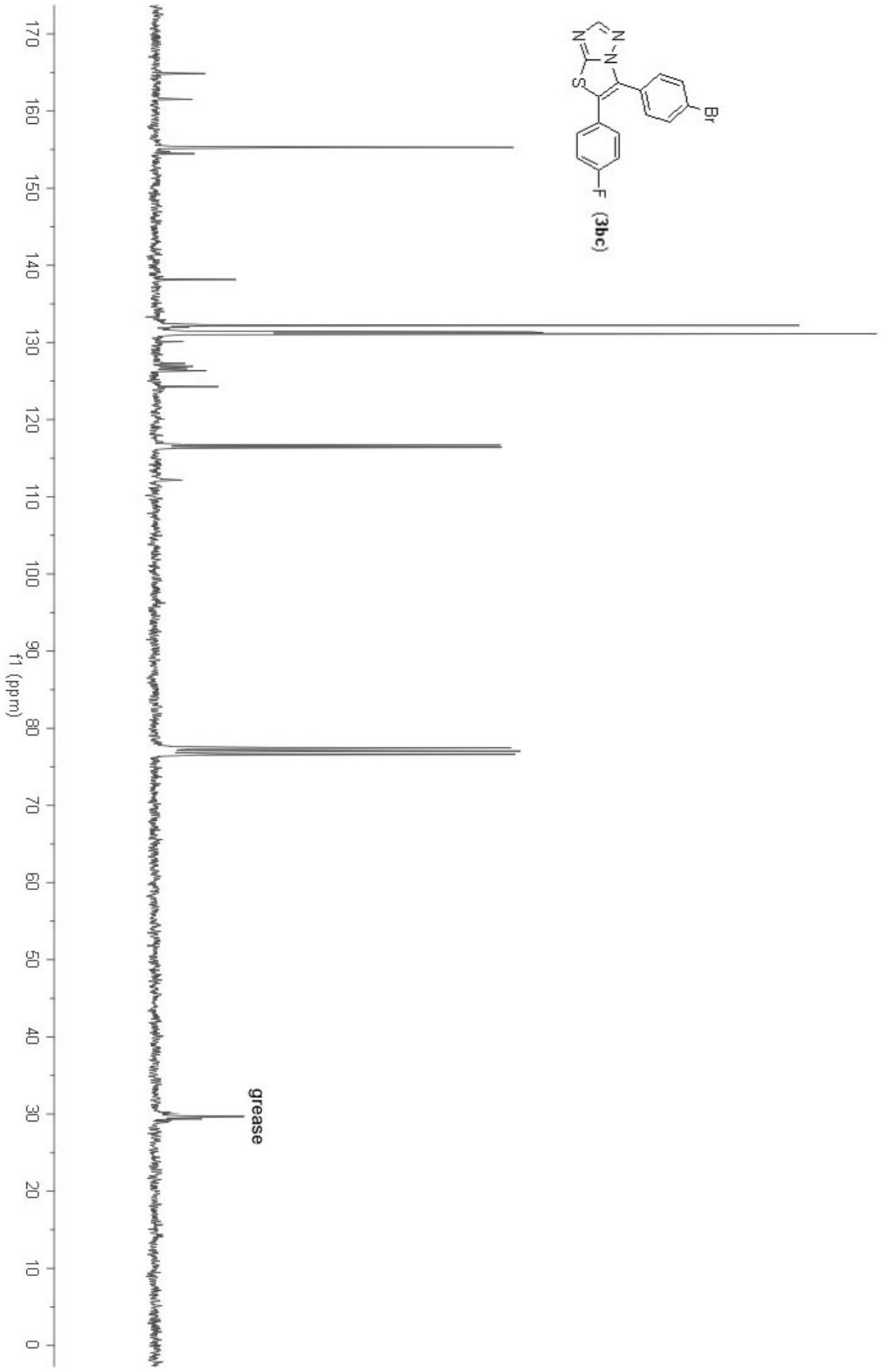
[^{13}C NMR Spectra of **3bc**]



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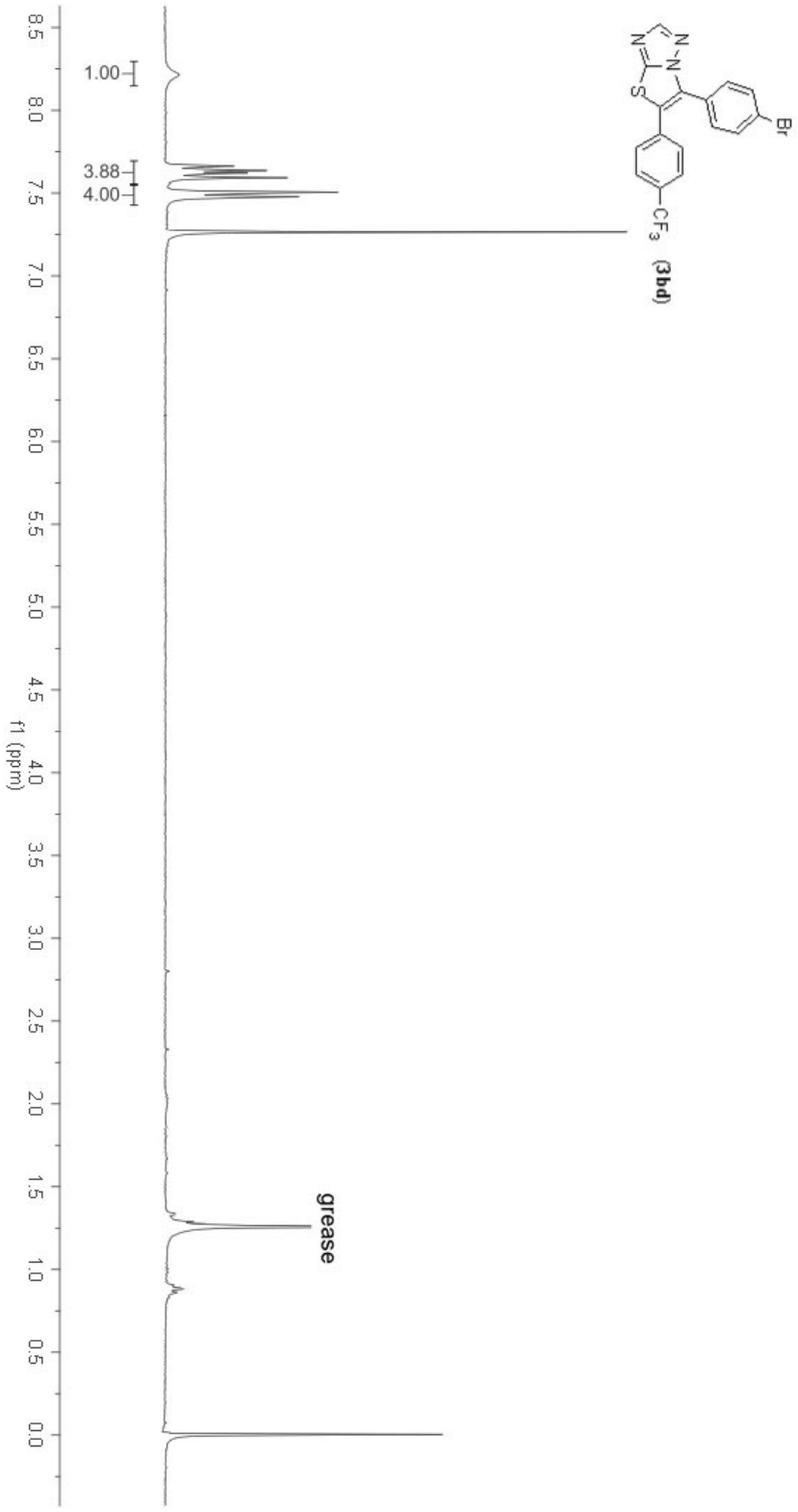
[^{1}H NMR Spectra of **3bd**]



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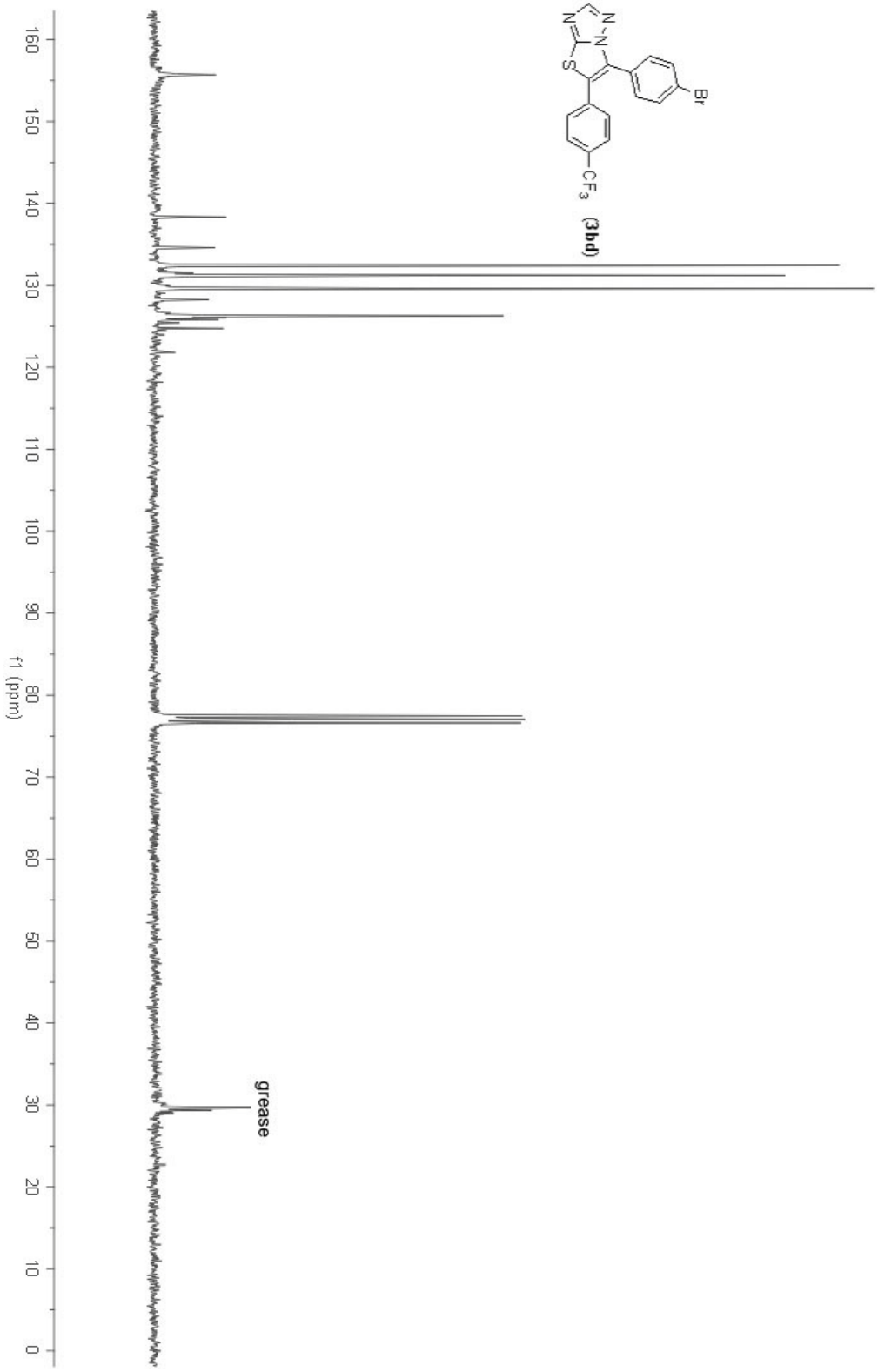
[^{13}C NMR Spectra of **3bd**]



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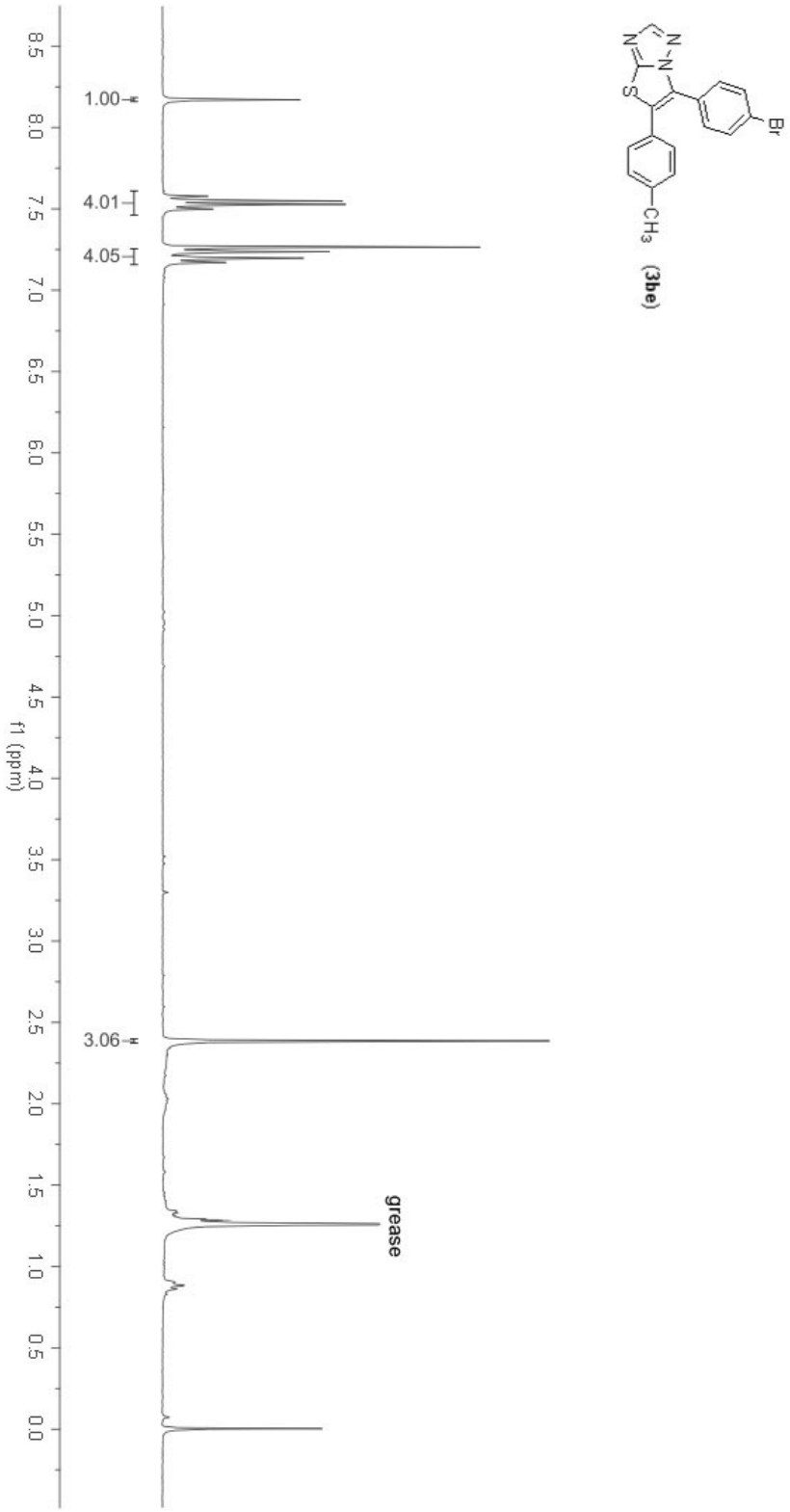
[^{1}H NMR Spectra of **3be**]



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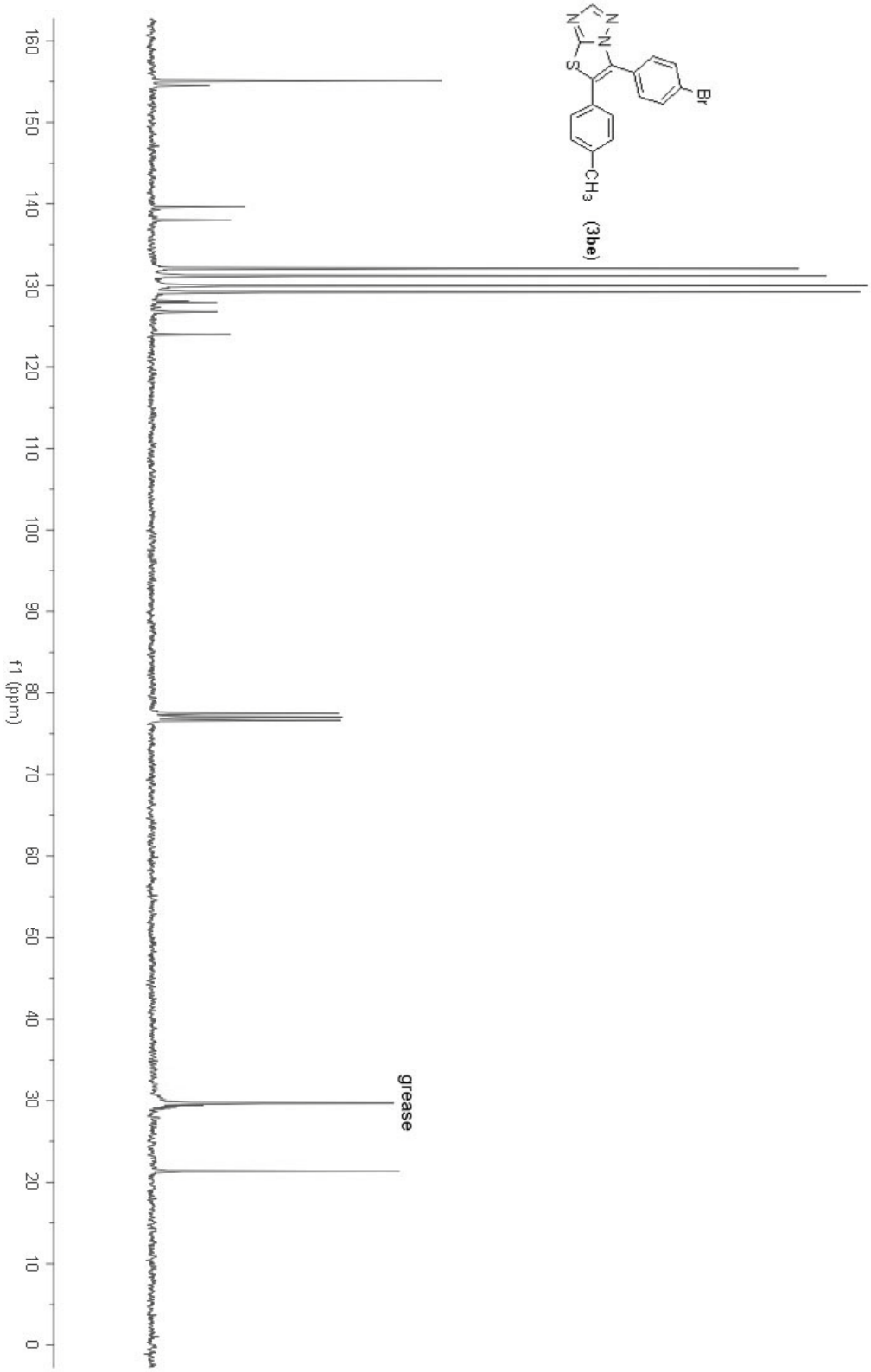
[^{13}C NMR Spectra of **3be**]



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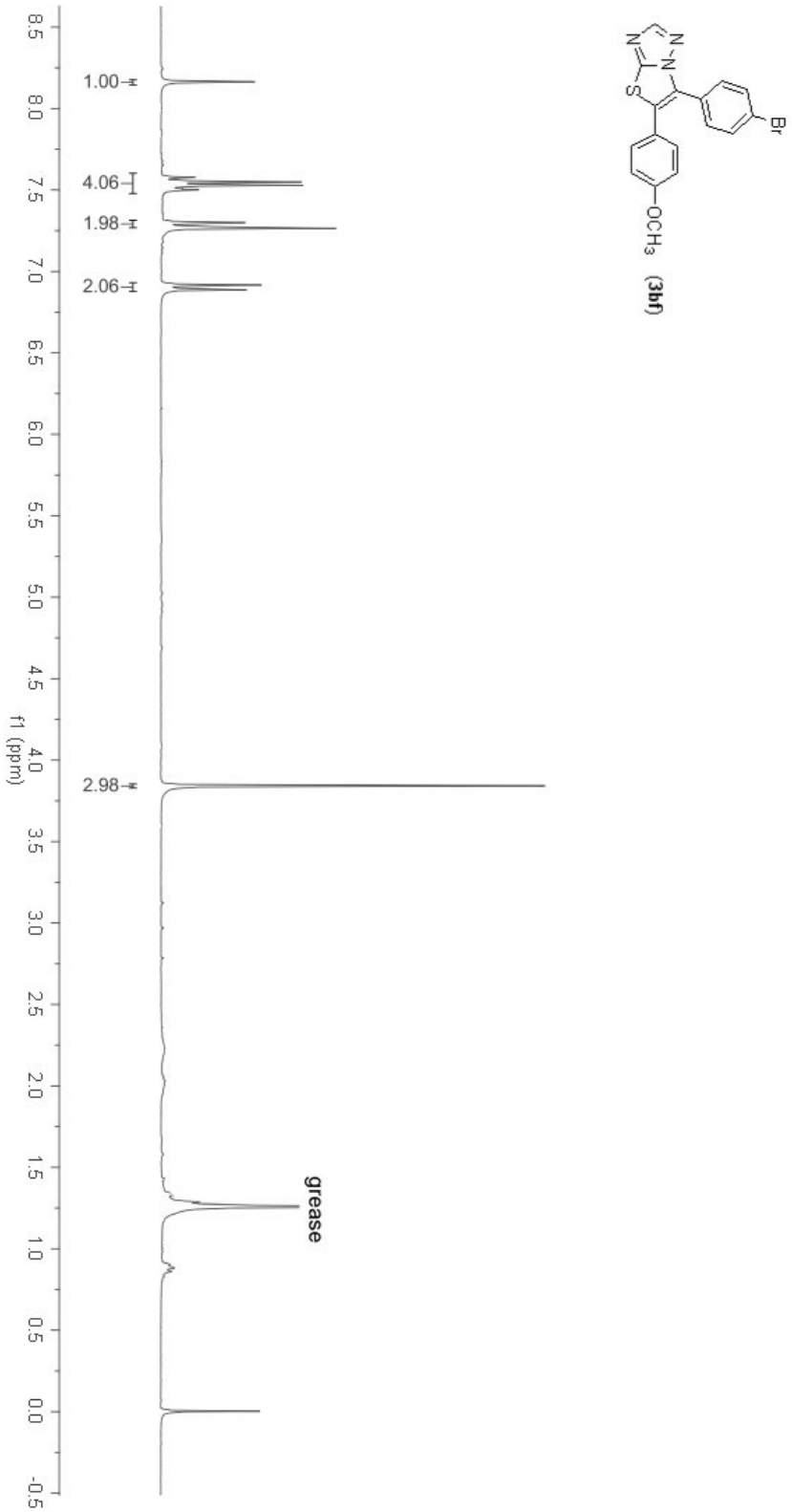
[^{1}H NMR Spectra of **3bf**]



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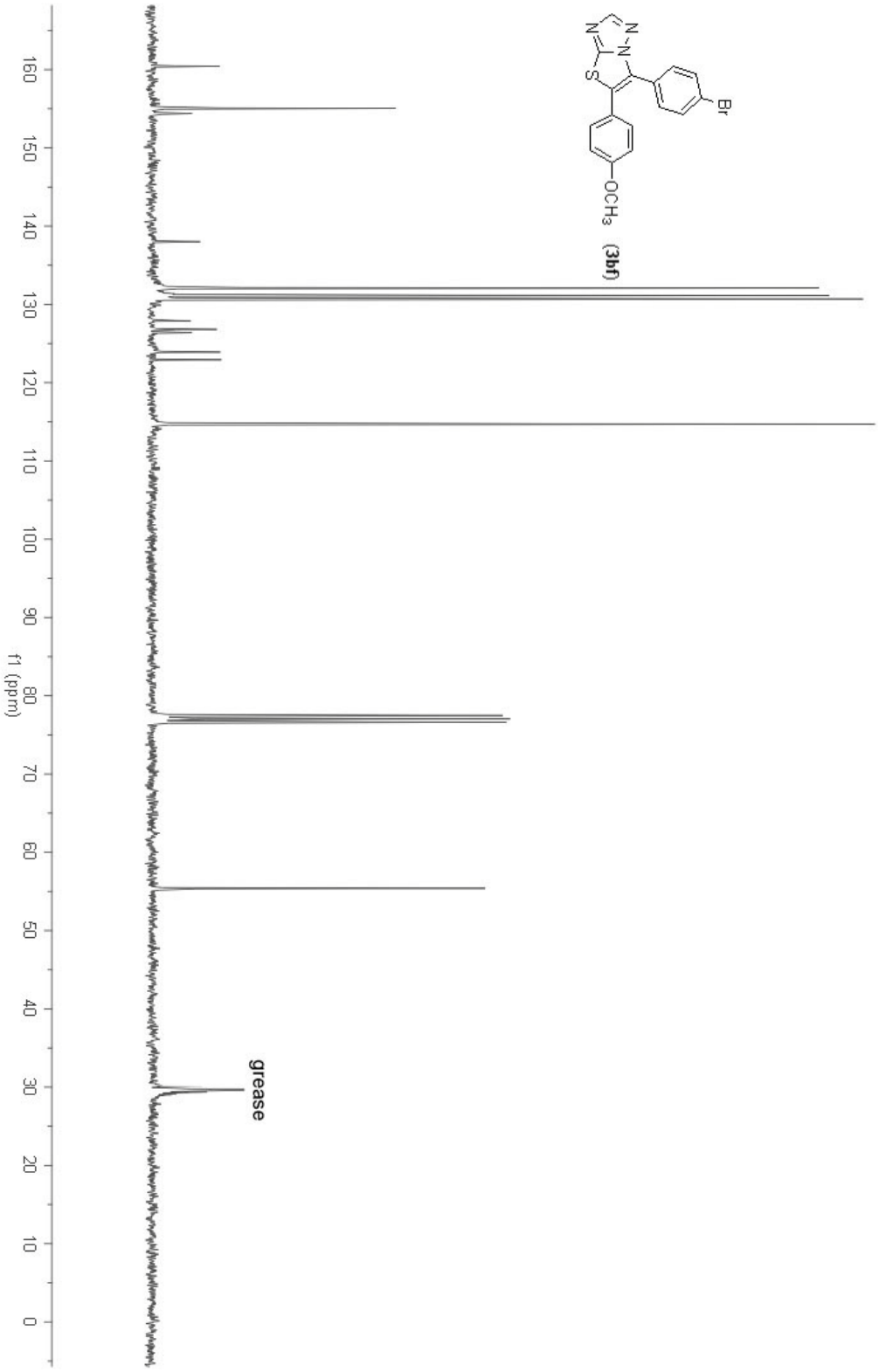
[^{13}C NMR Spectra of **3bf**]



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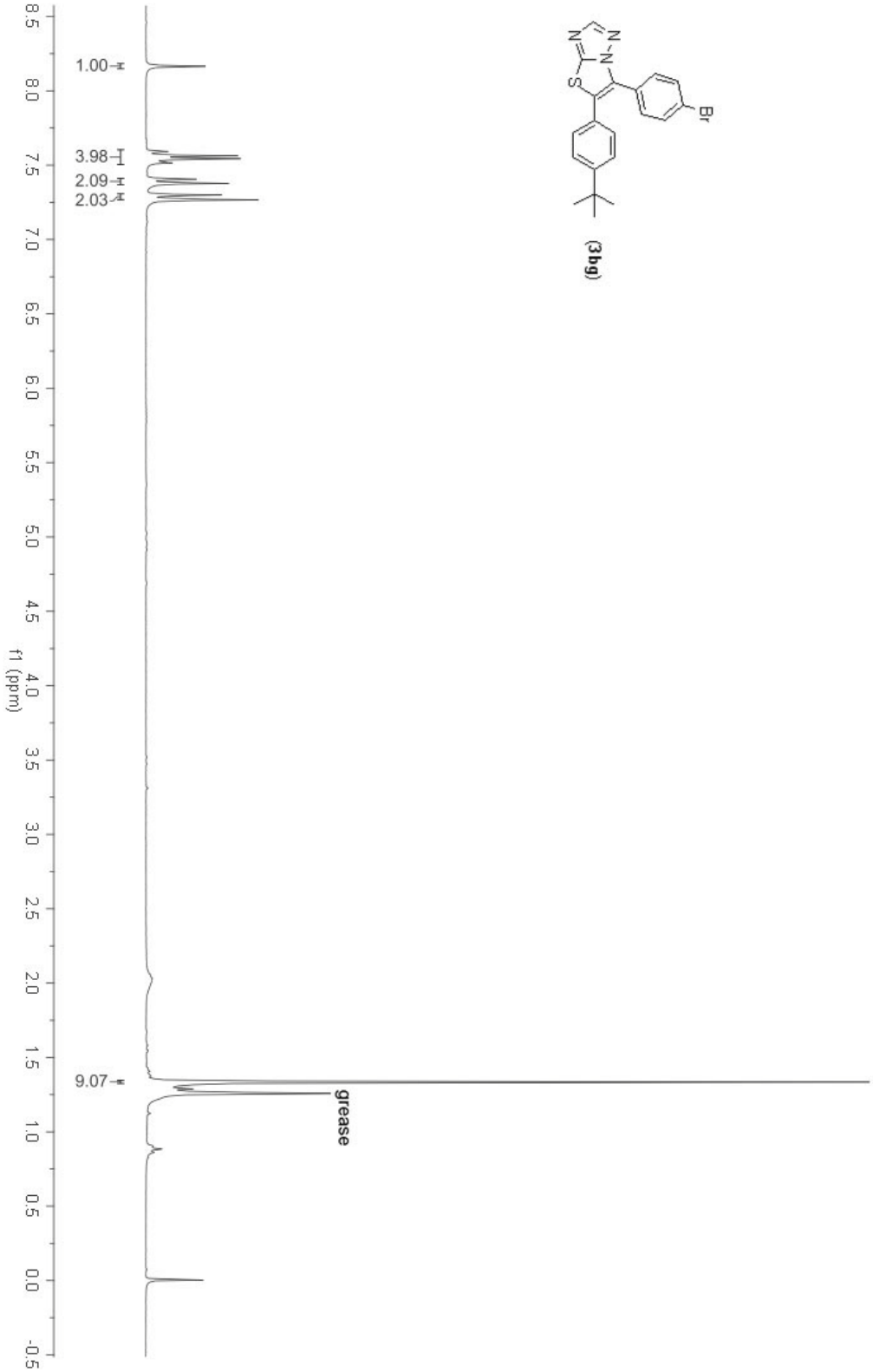
[^{1}H NMR Spectra of **3bg**]



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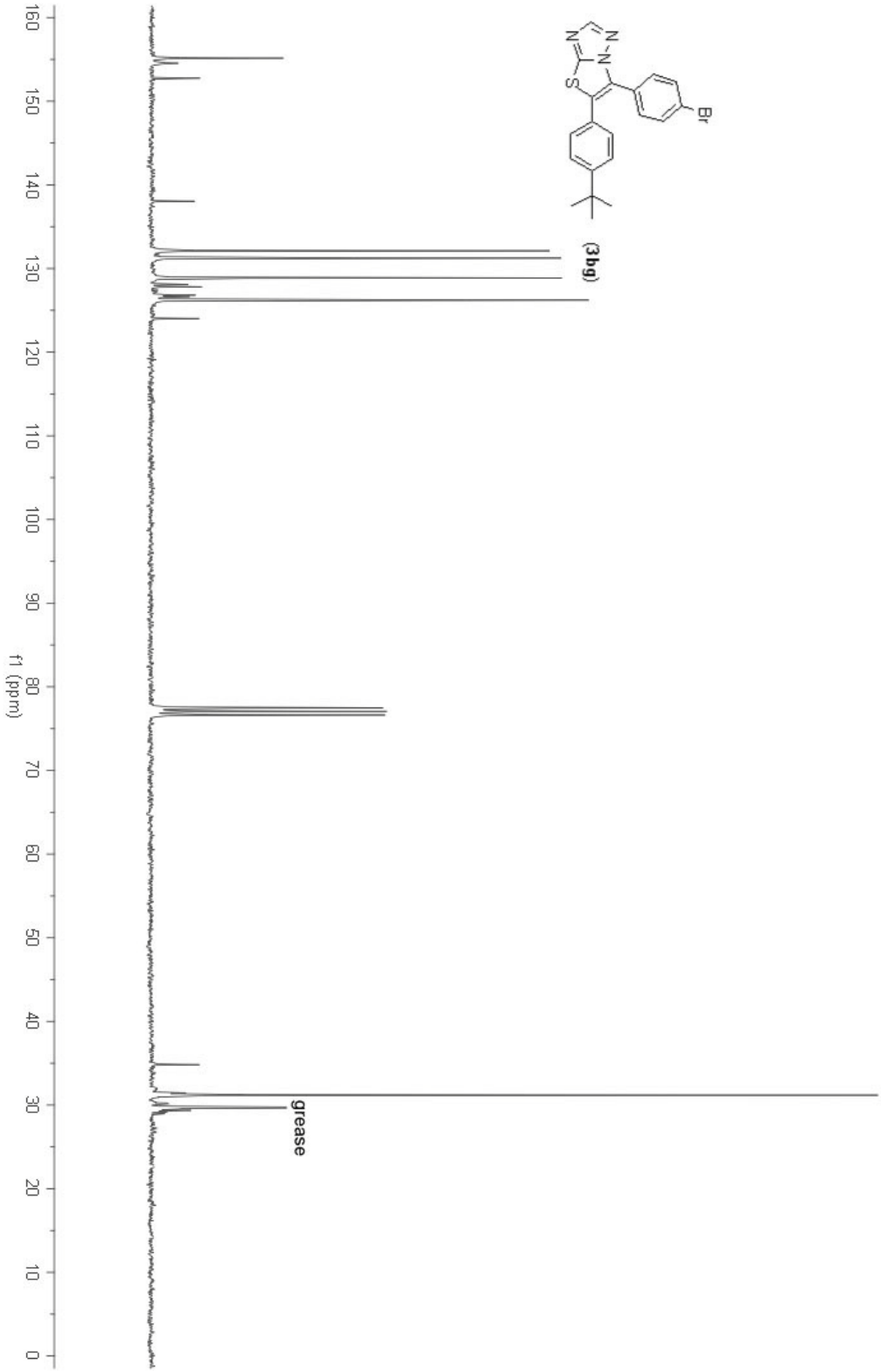
[^{13}C NMR Spectra of **3bg**]



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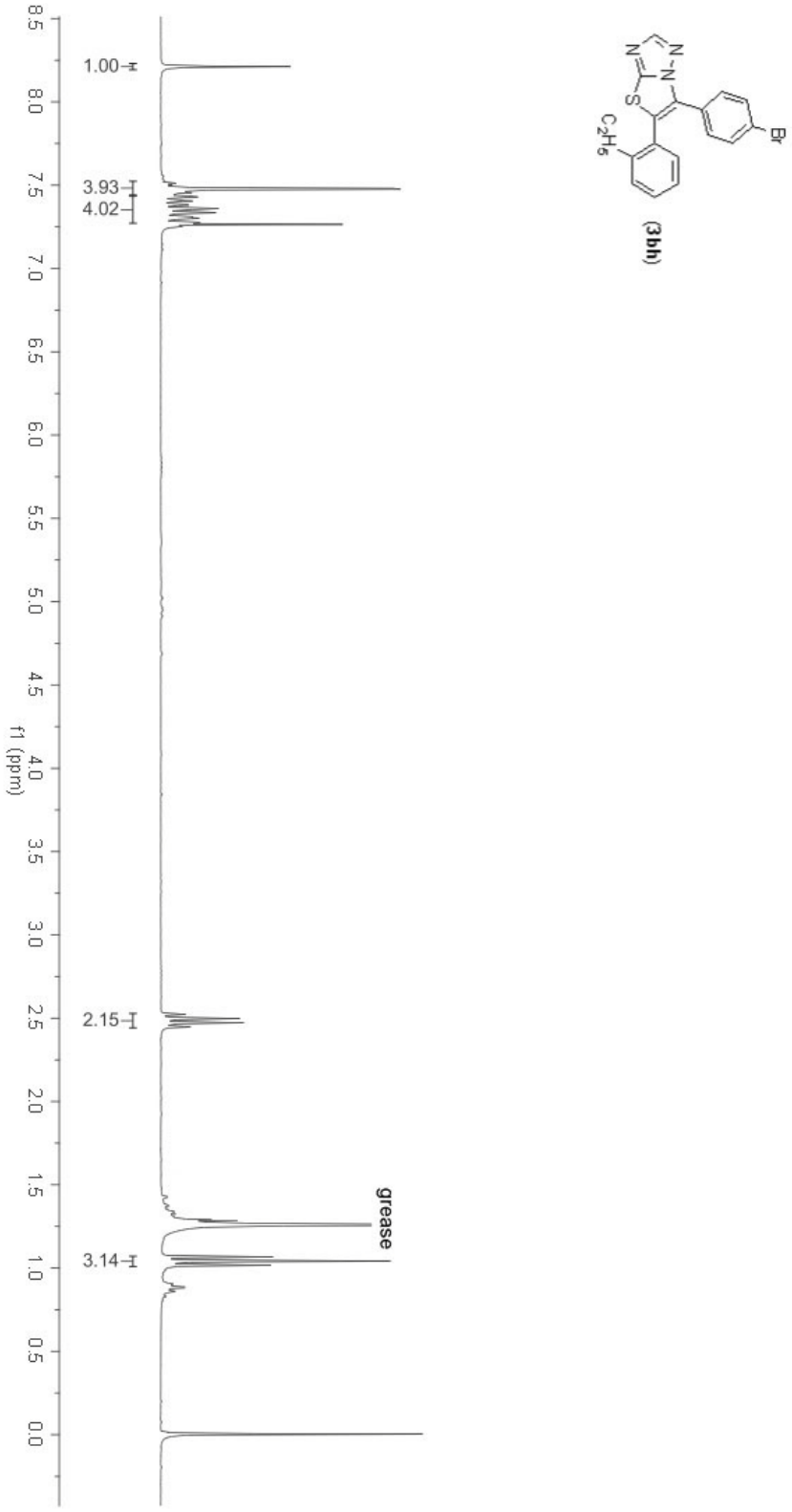
[^{1}H NMR Spectra of **3bh**]



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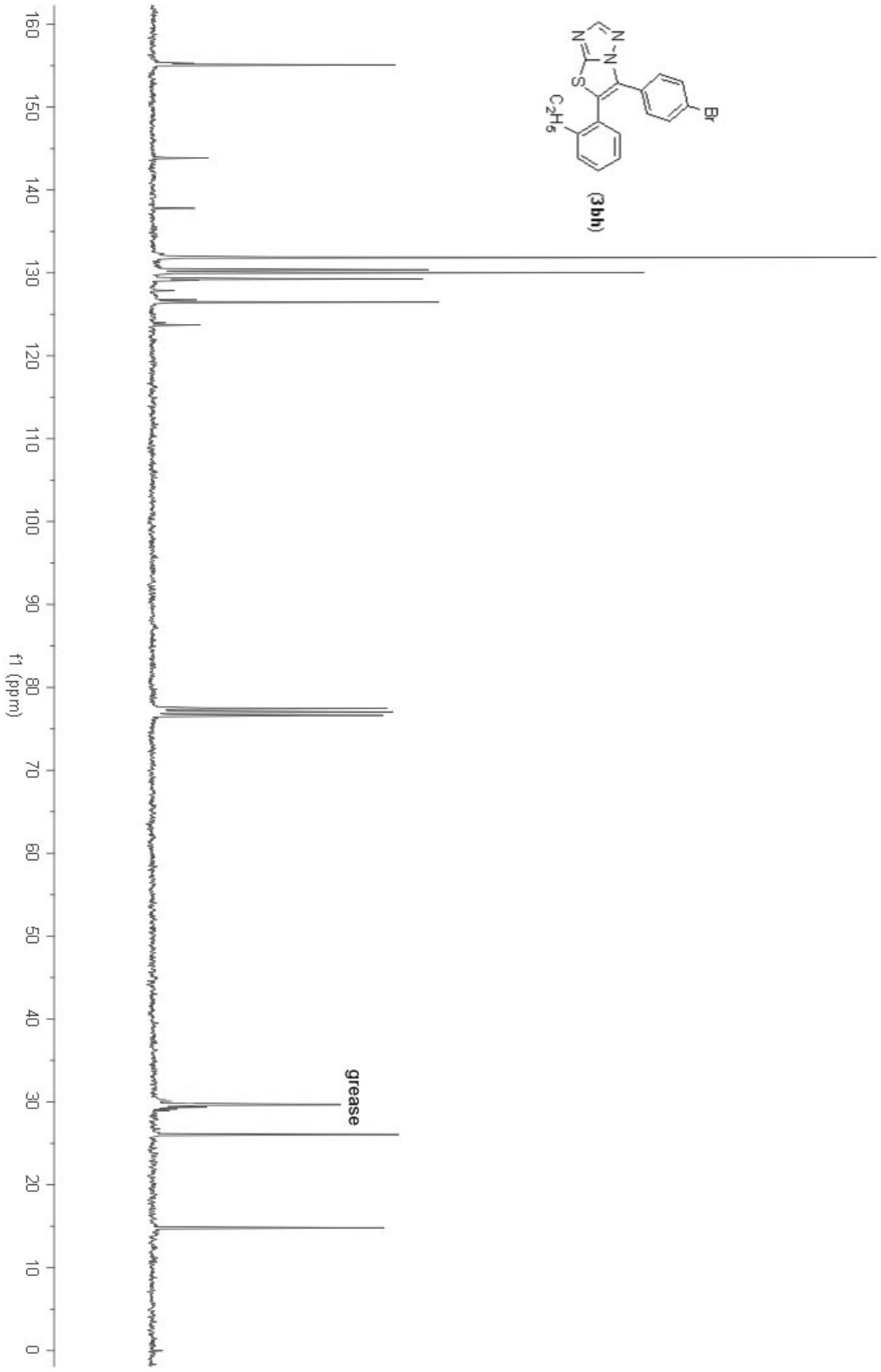
[^{13}C NMR Spectra of **3bh**]



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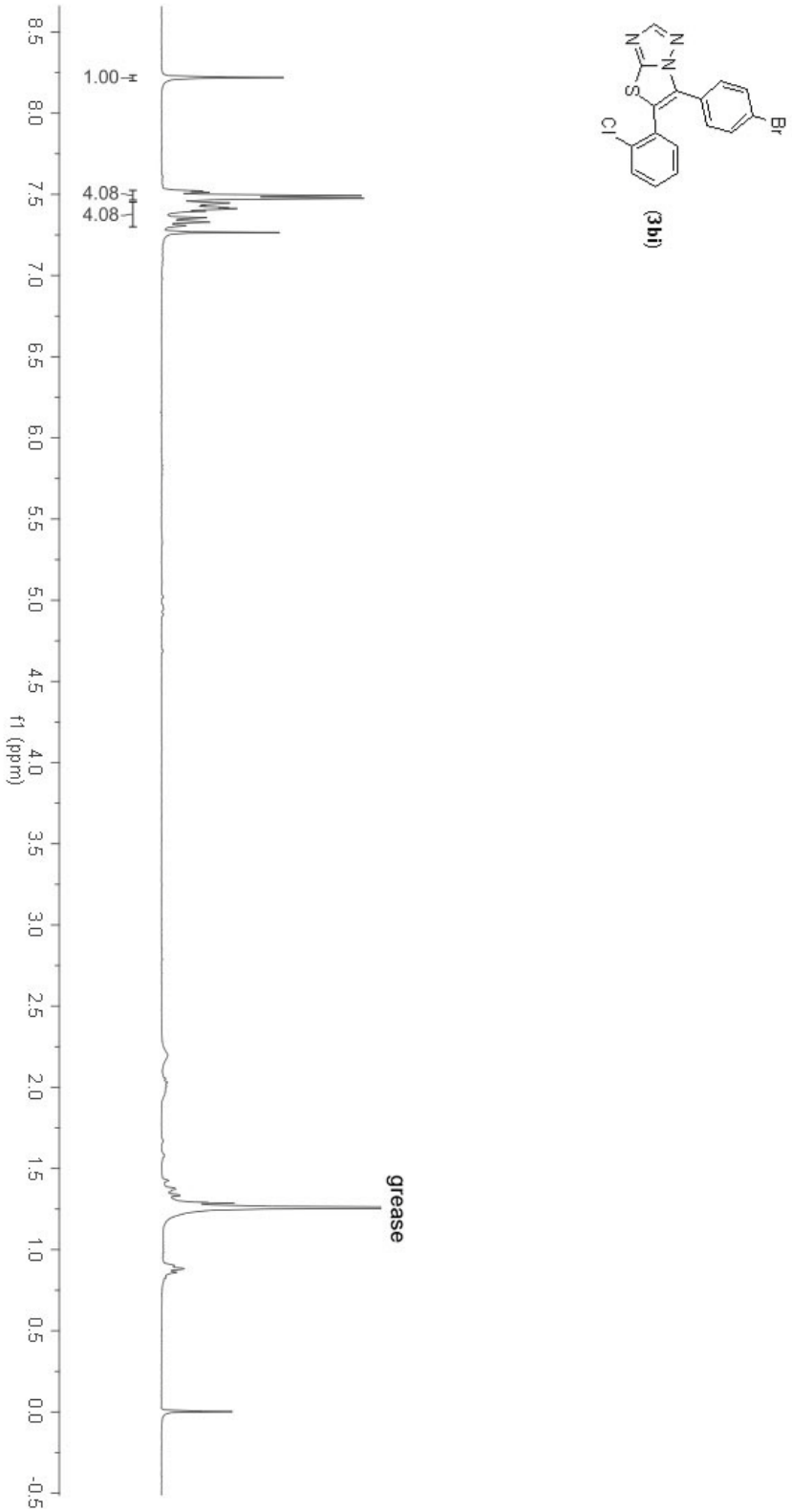
[^{1}H NMR Spectra of **3bi**]



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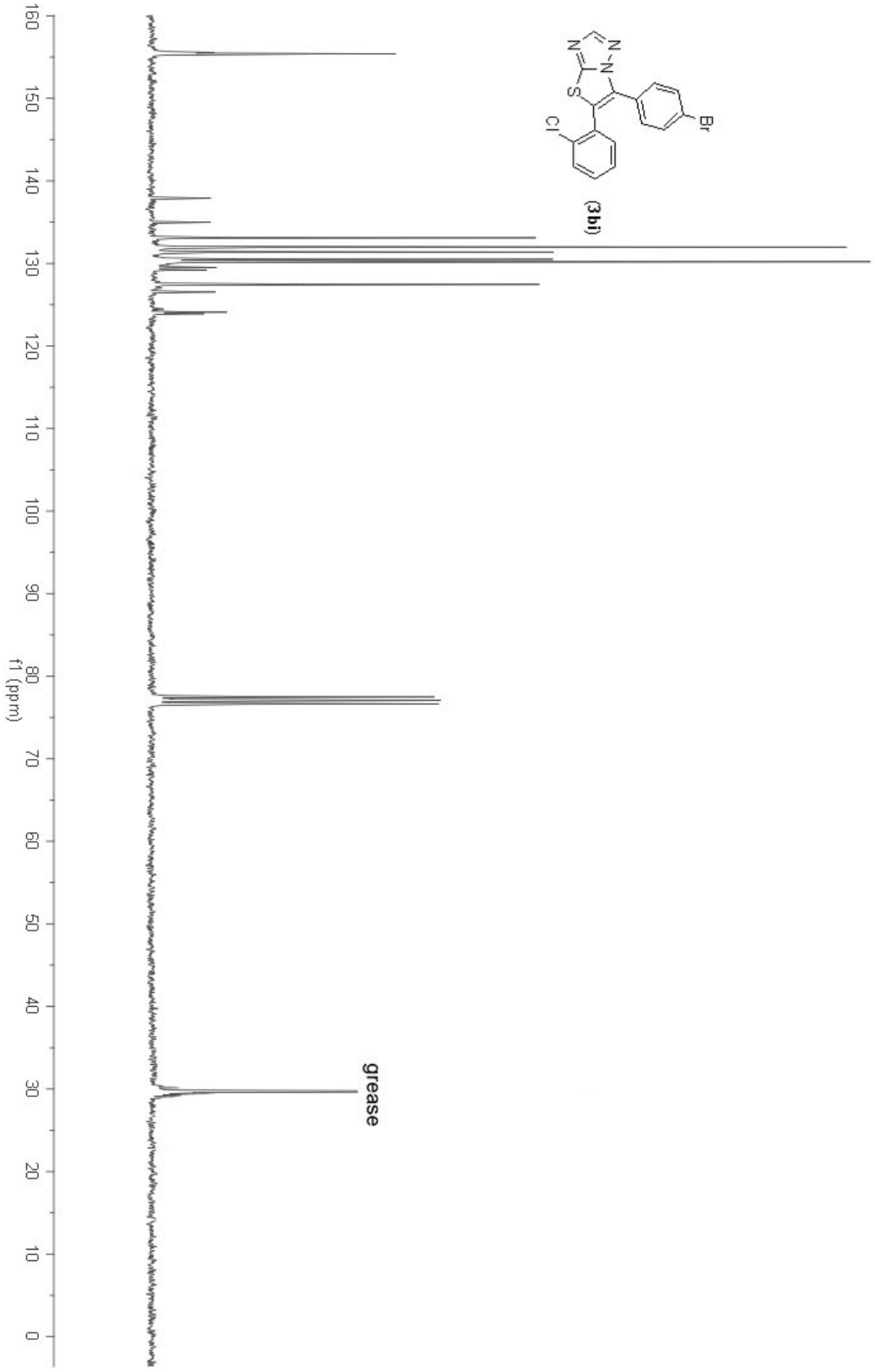
[^{13}C NMR Spectra of **3bi**]



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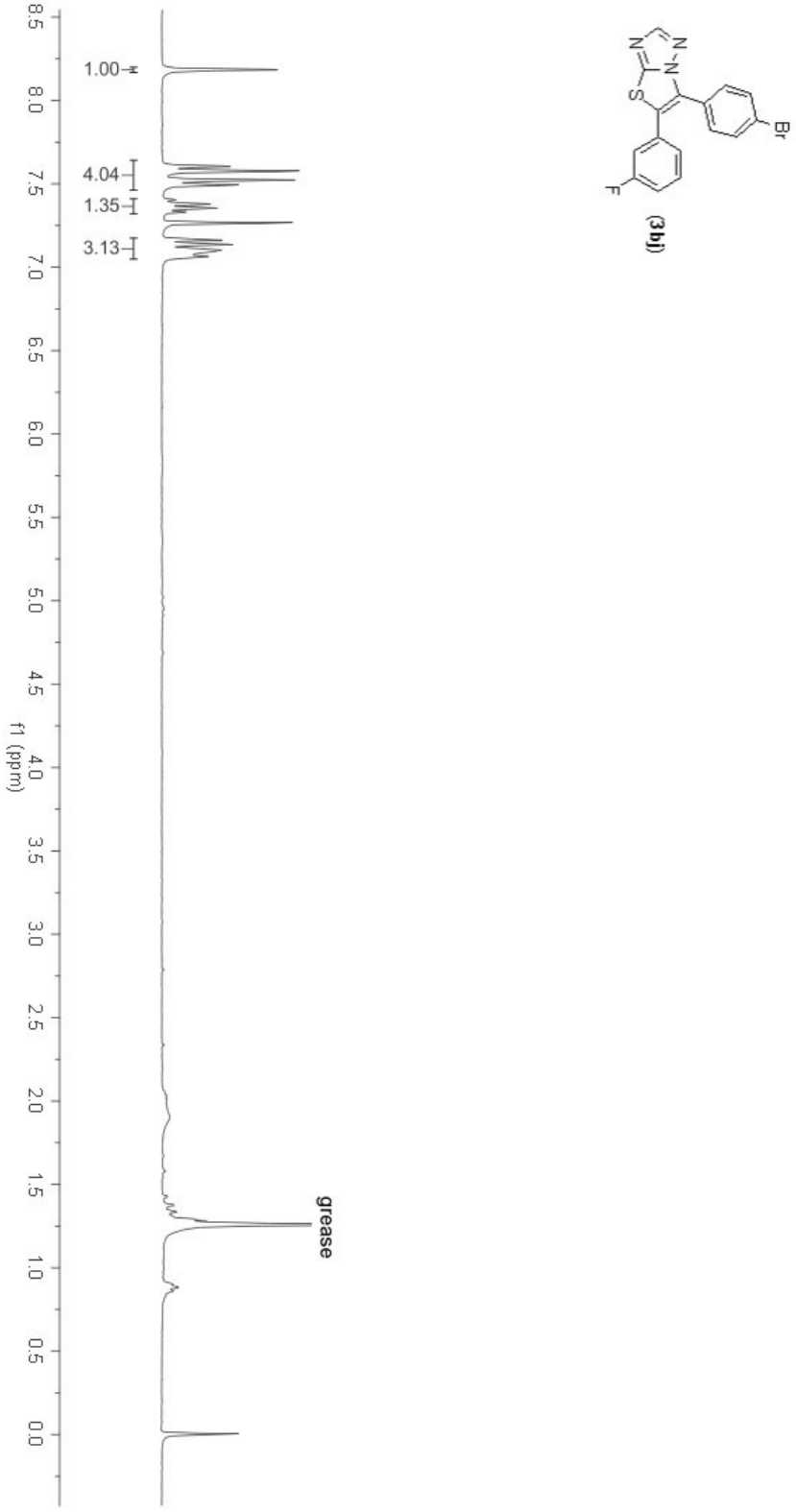
[^{1}H NMR Spectra of **3bj**]



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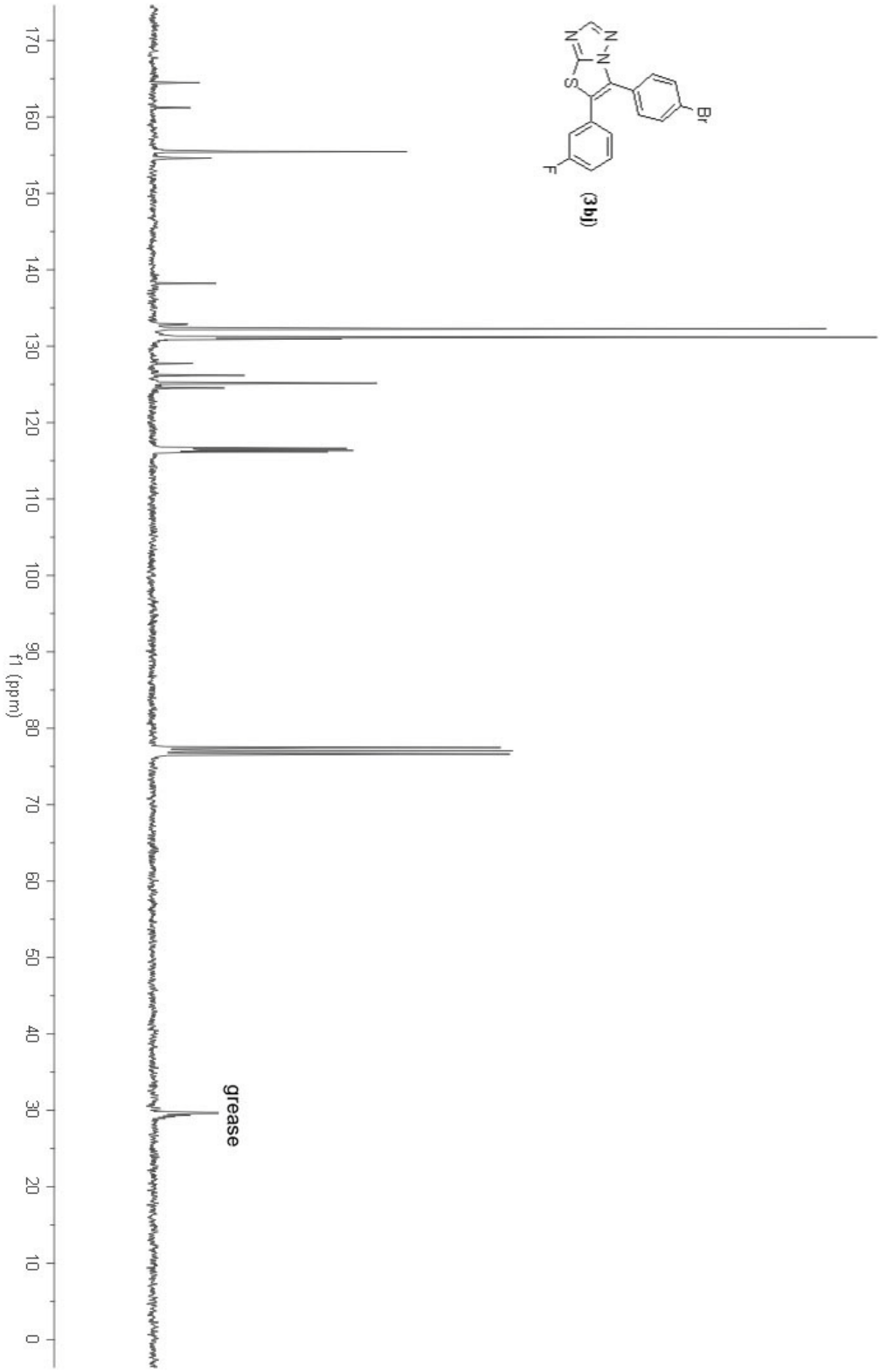
[^{13}C NMR Spectra of **3bj**]



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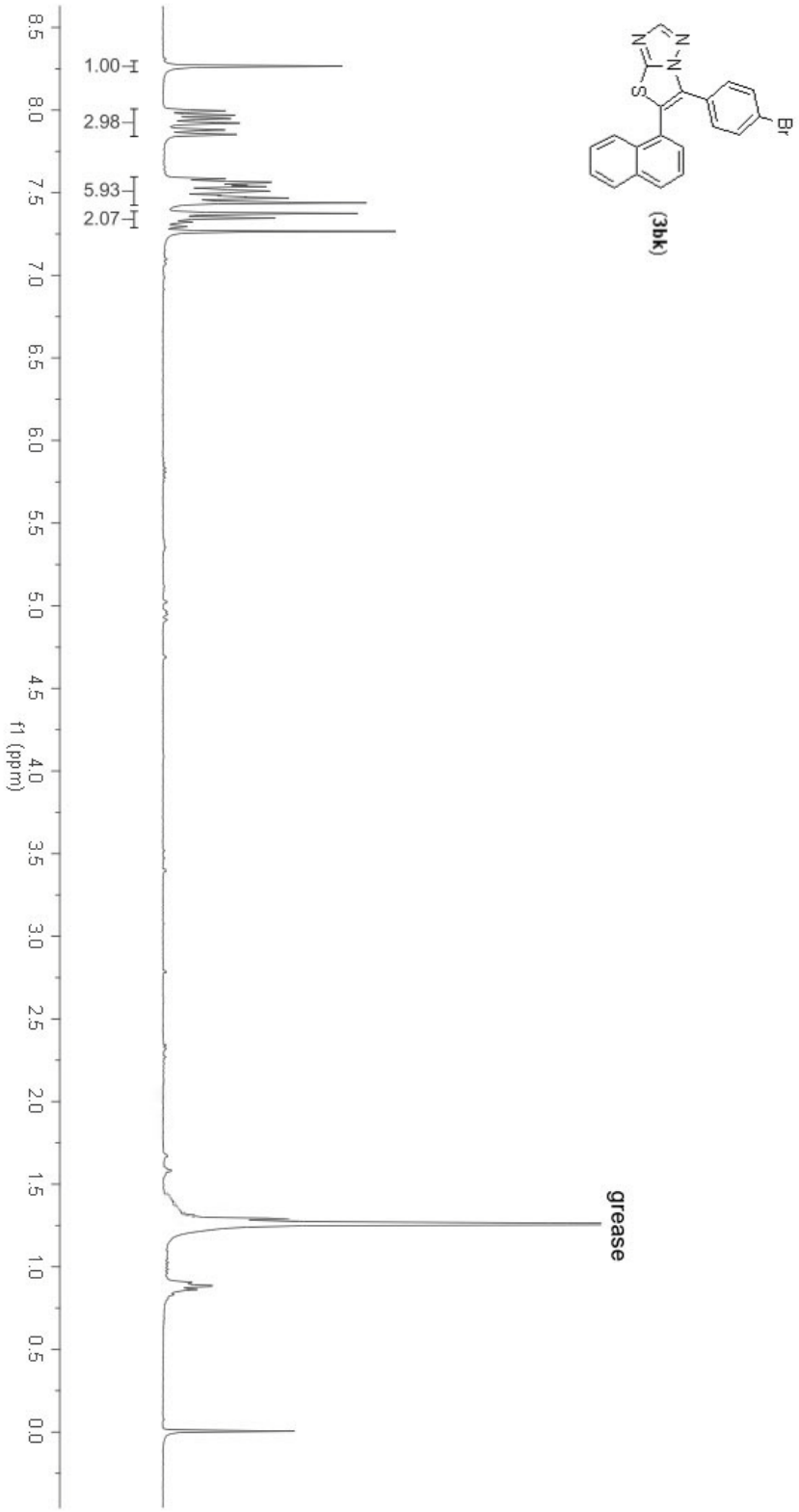
[^{1}H NMR Spectra of **3bk**]



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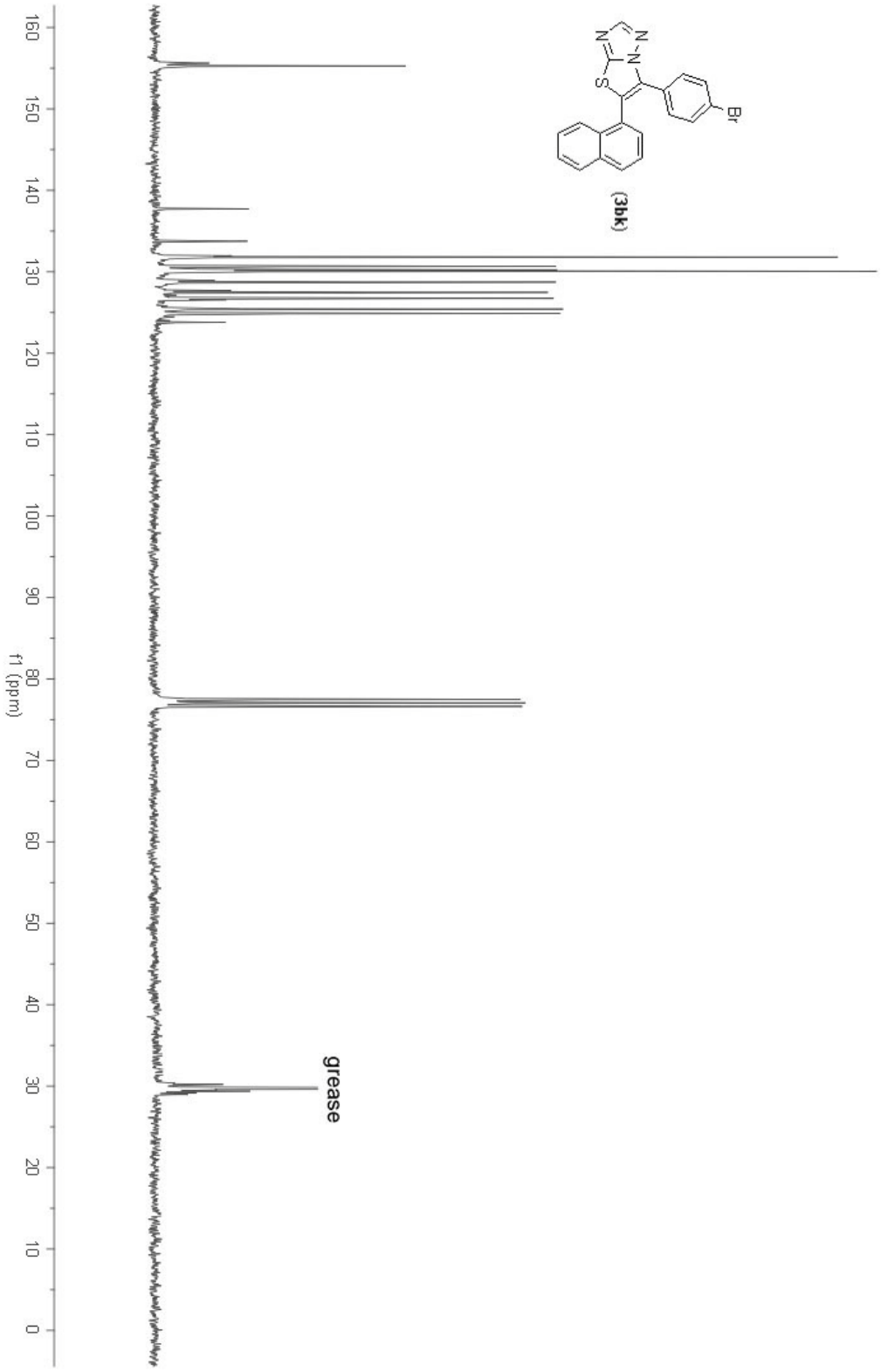
[^{13}C NMR Spectra of **3bk**]



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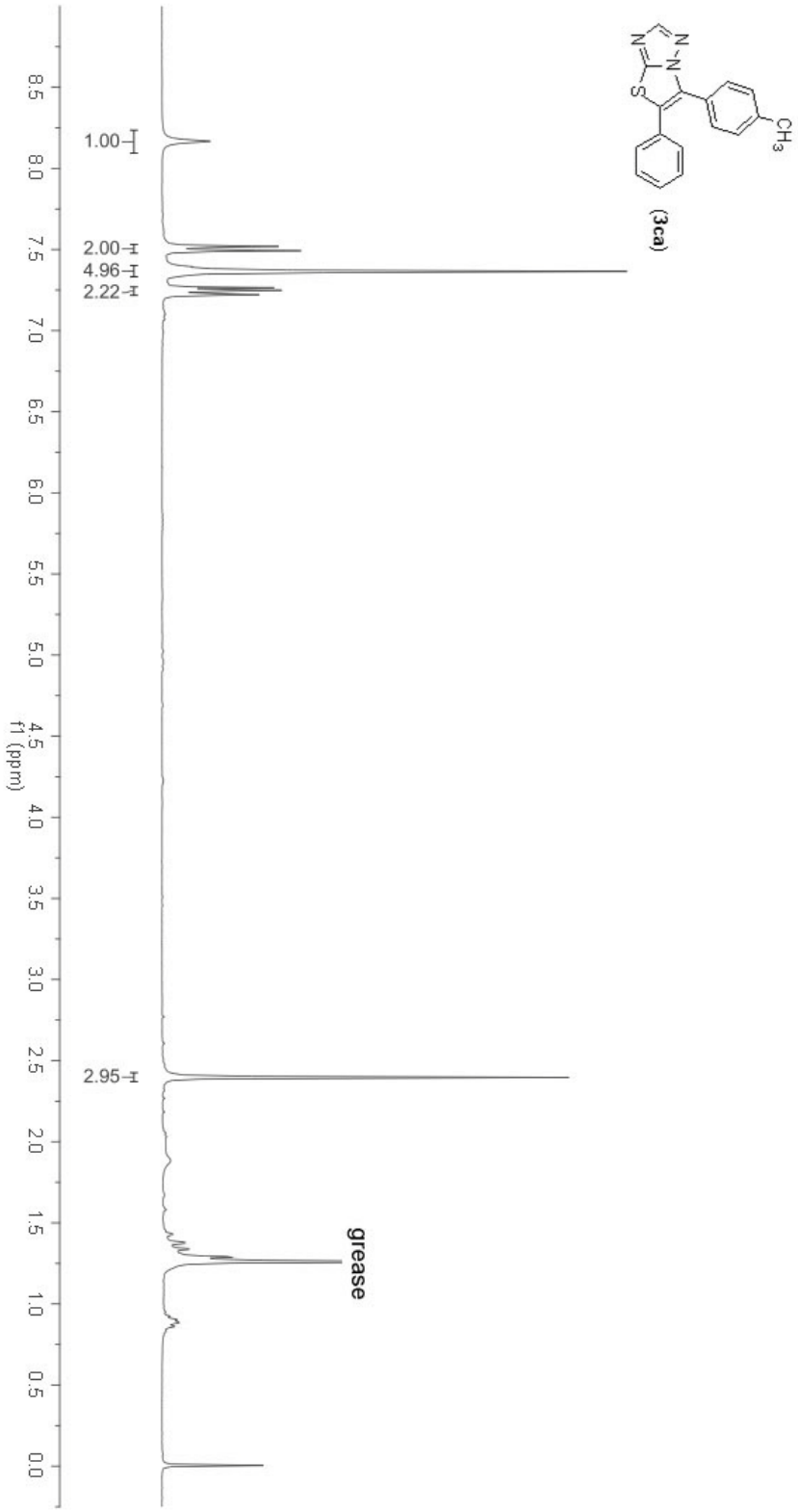
[^{1}H NMR Spectra of **3ca**]



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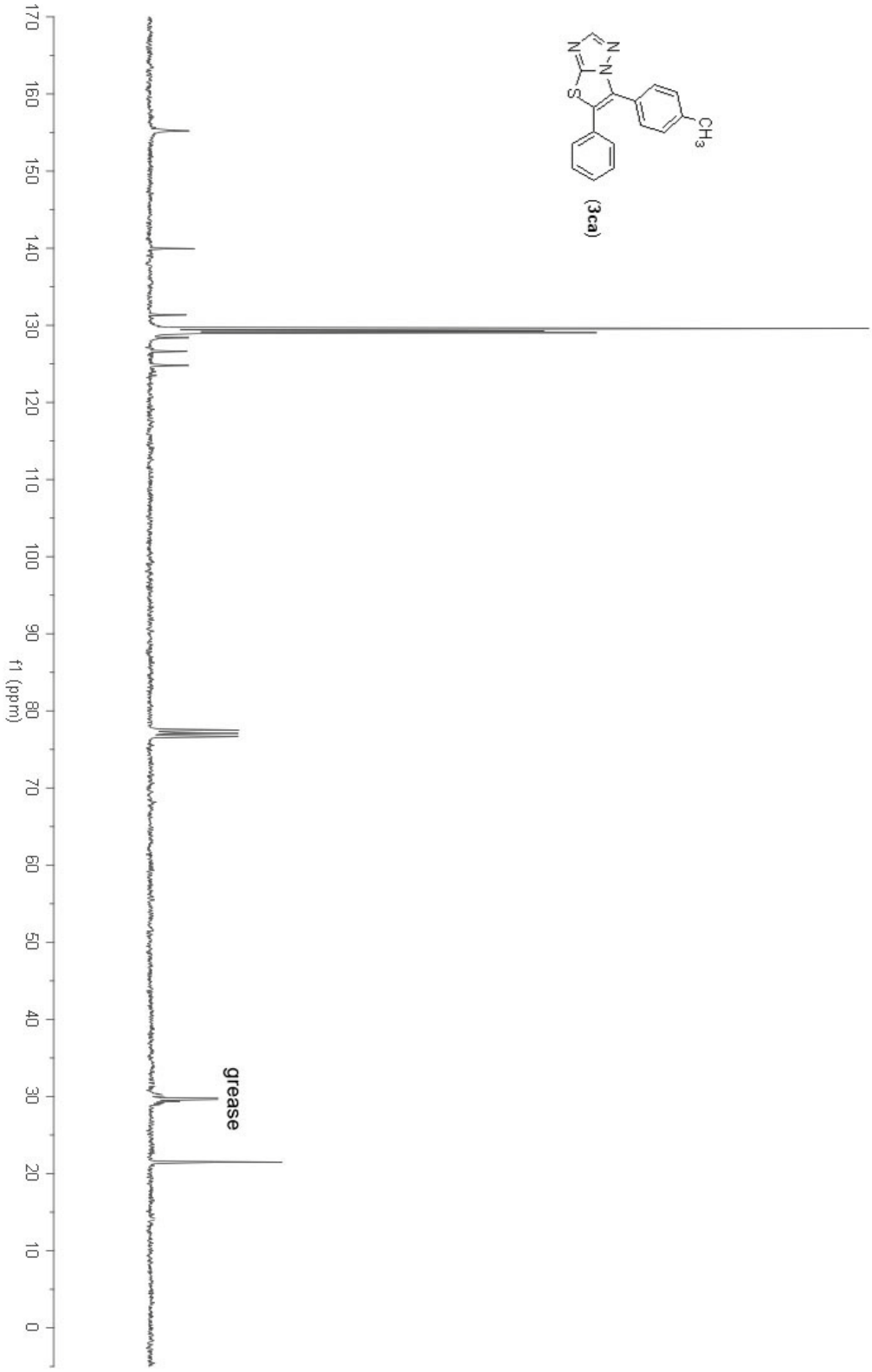
[^{13}C NMR Spectra of **3ca**]



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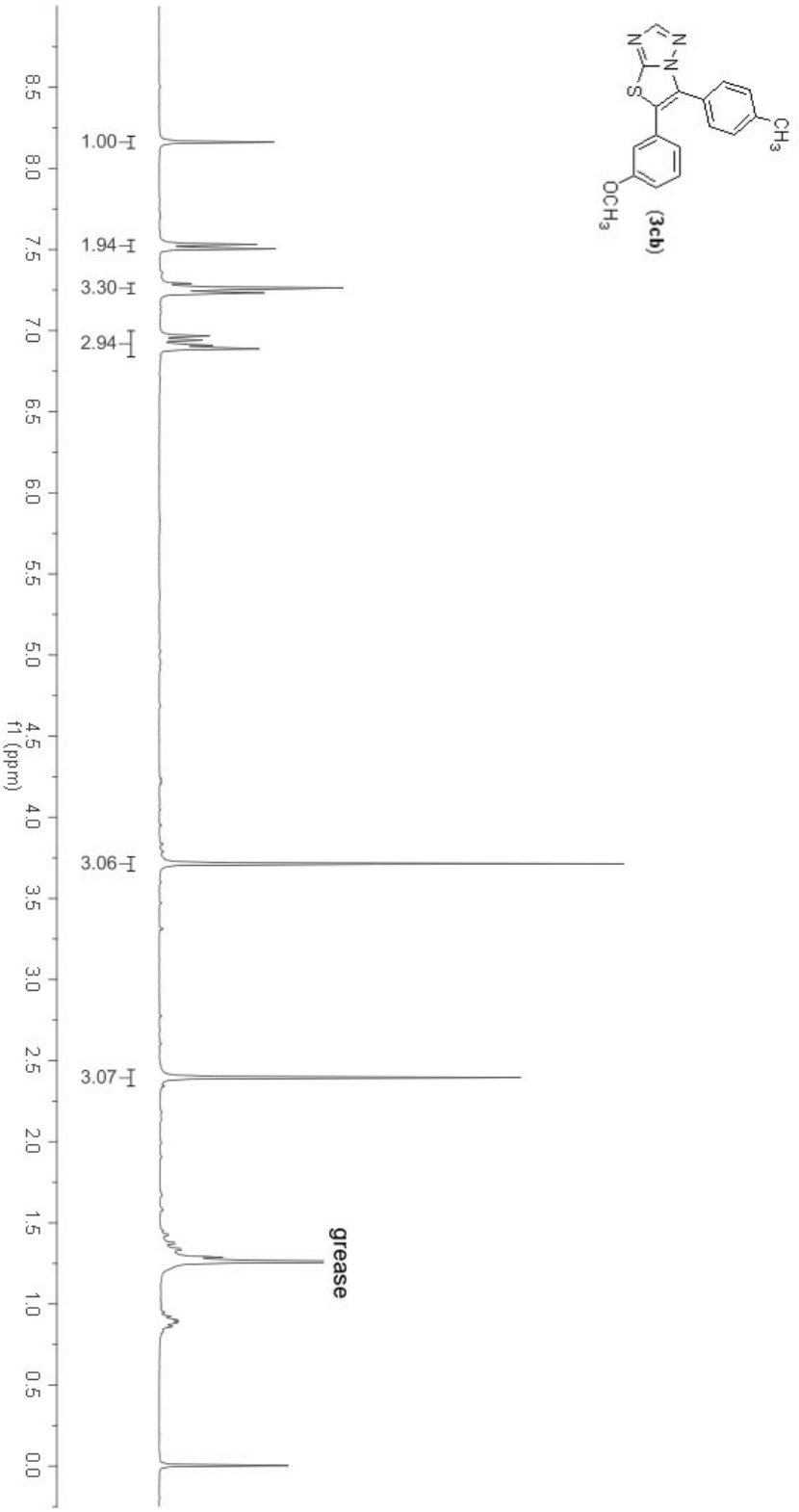
[^{1}H NMR Spectra of **3cb**]



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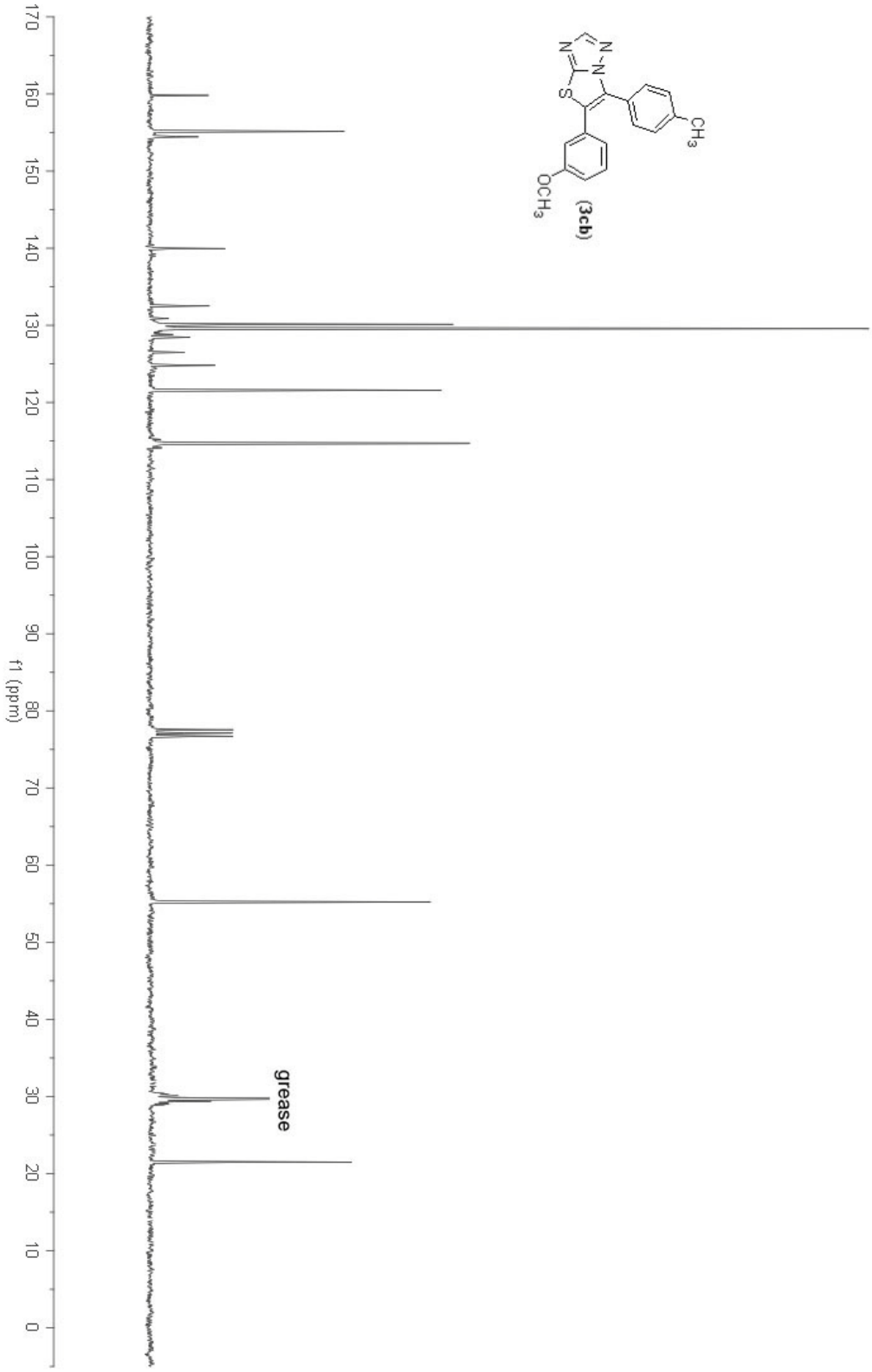
[^{13}C NMR Spectra of **3cb**]



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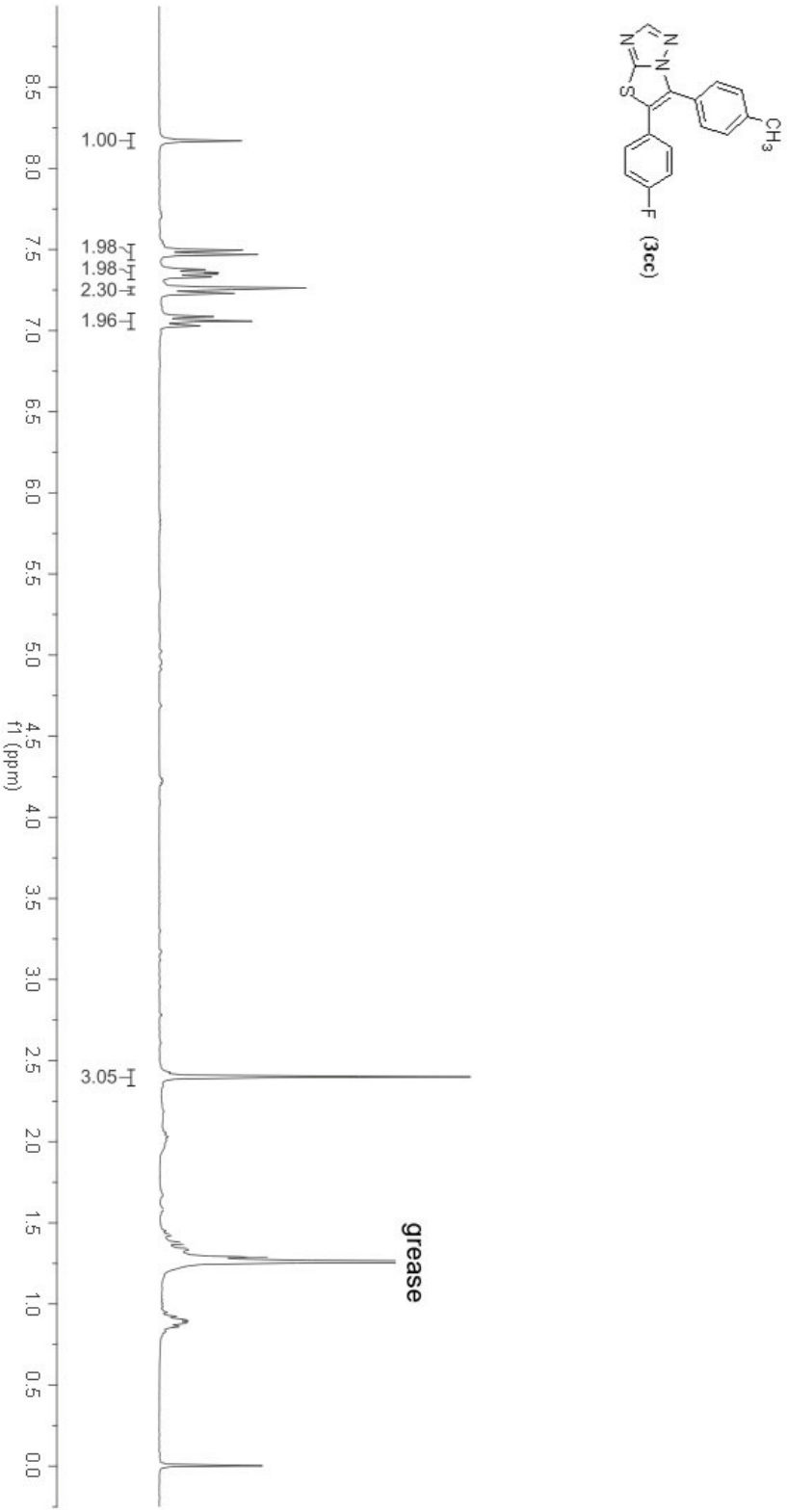
[^{1}H NMR Spectra of **3cc**]



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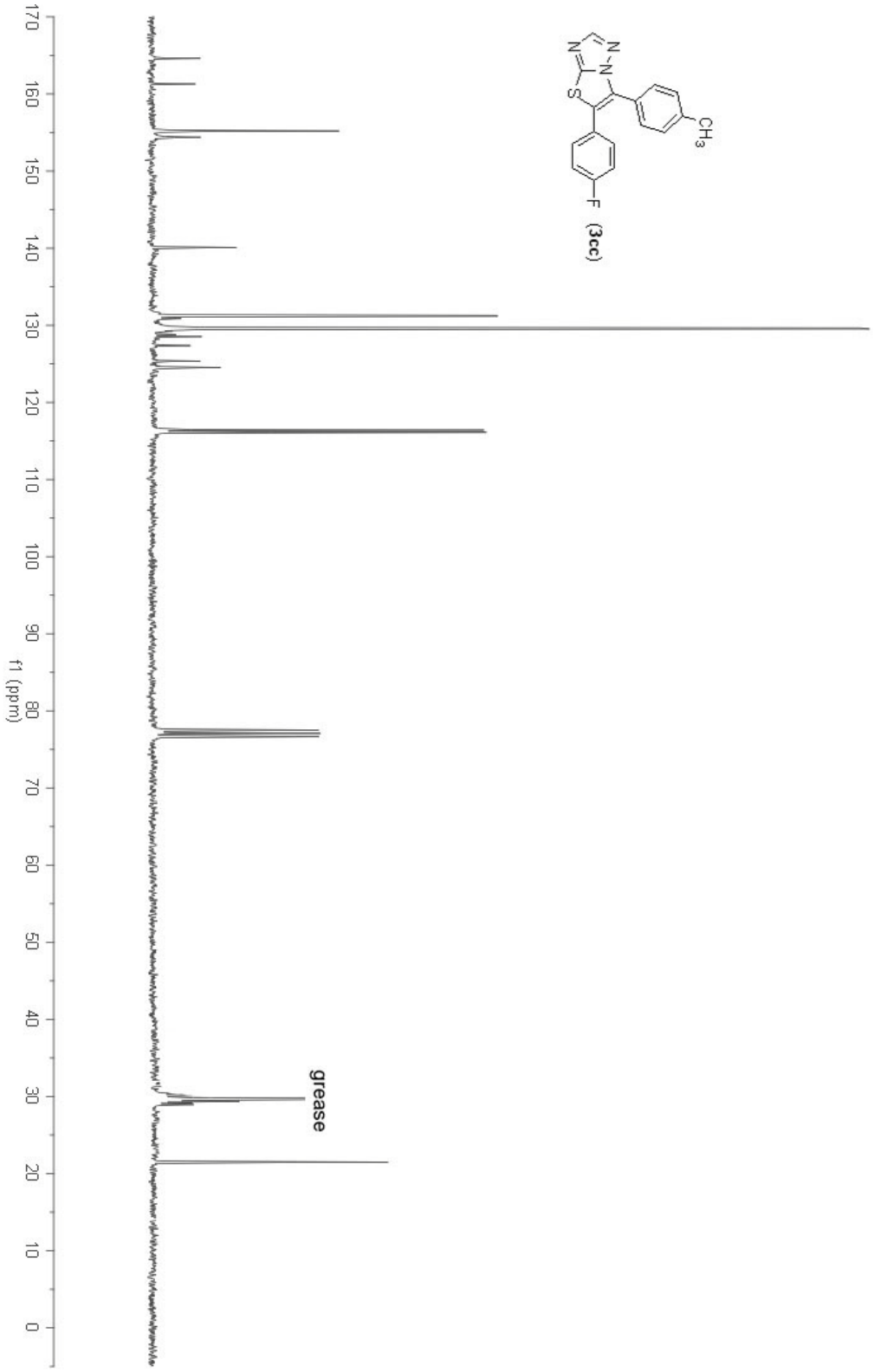
[^{13}C NMR Spectra of **3cc**]



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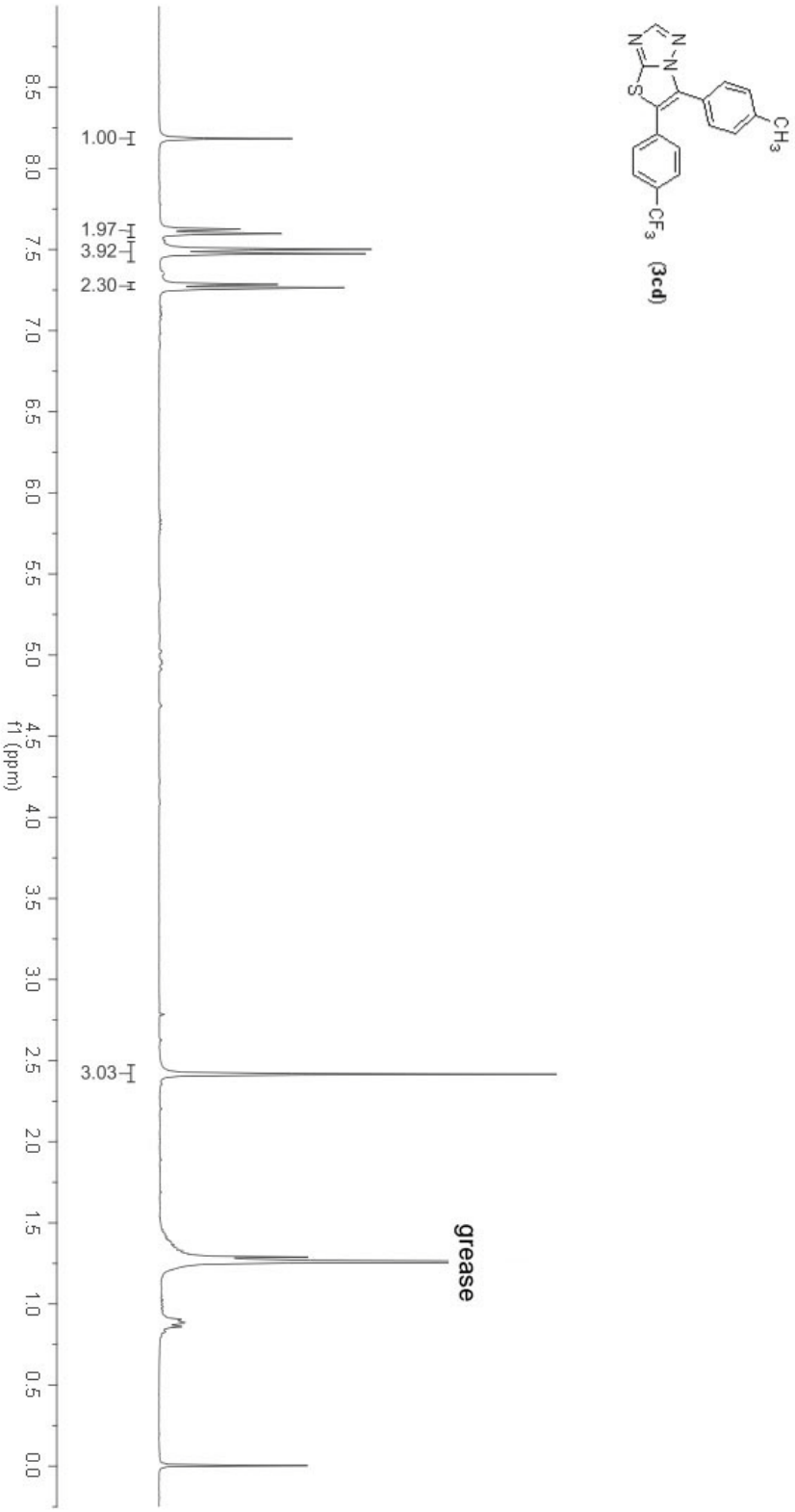
[^{1}H NMR Spectra of **3cd**]



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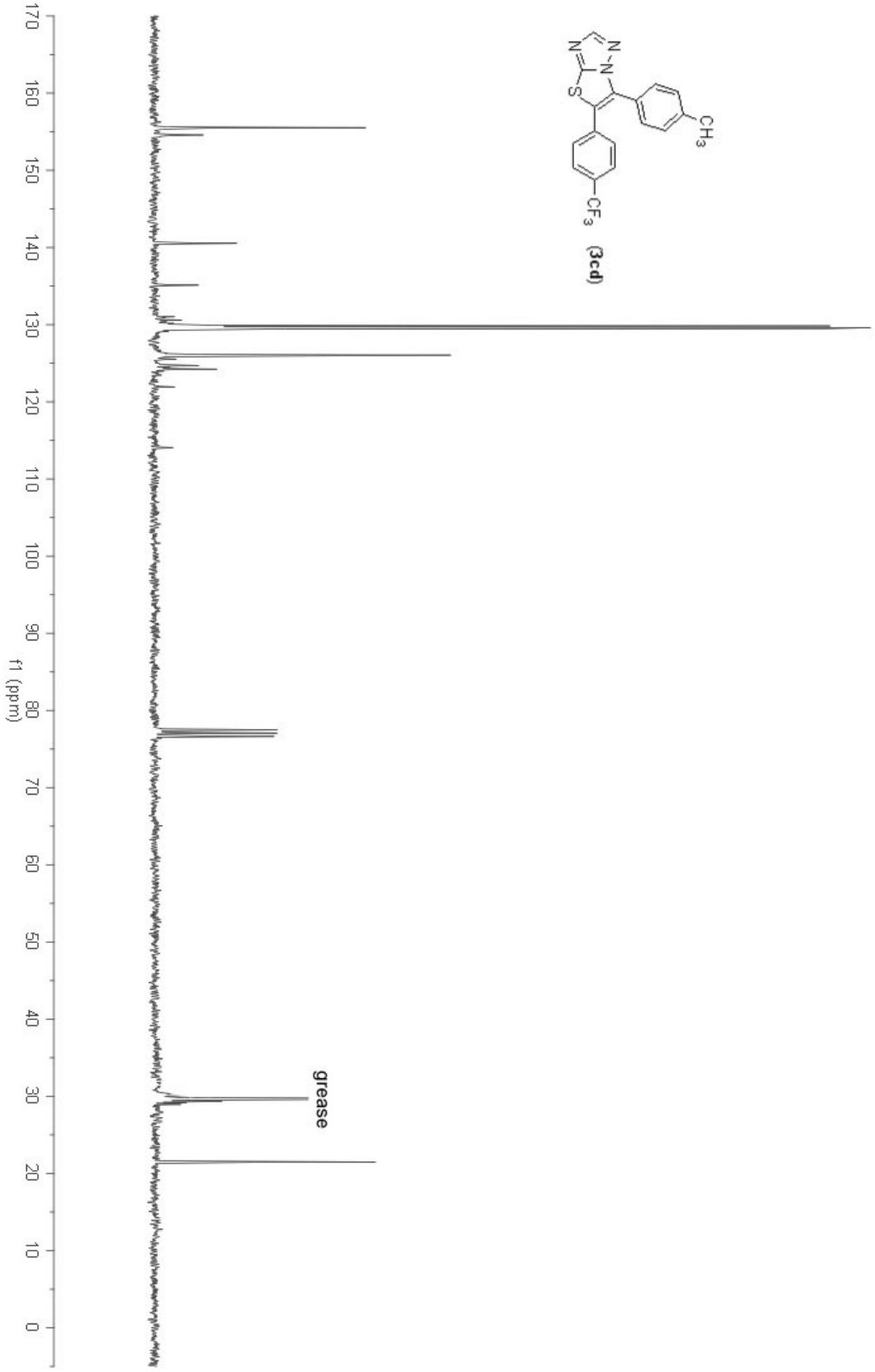
[^{13}C NMR Spectra of **3cd**]



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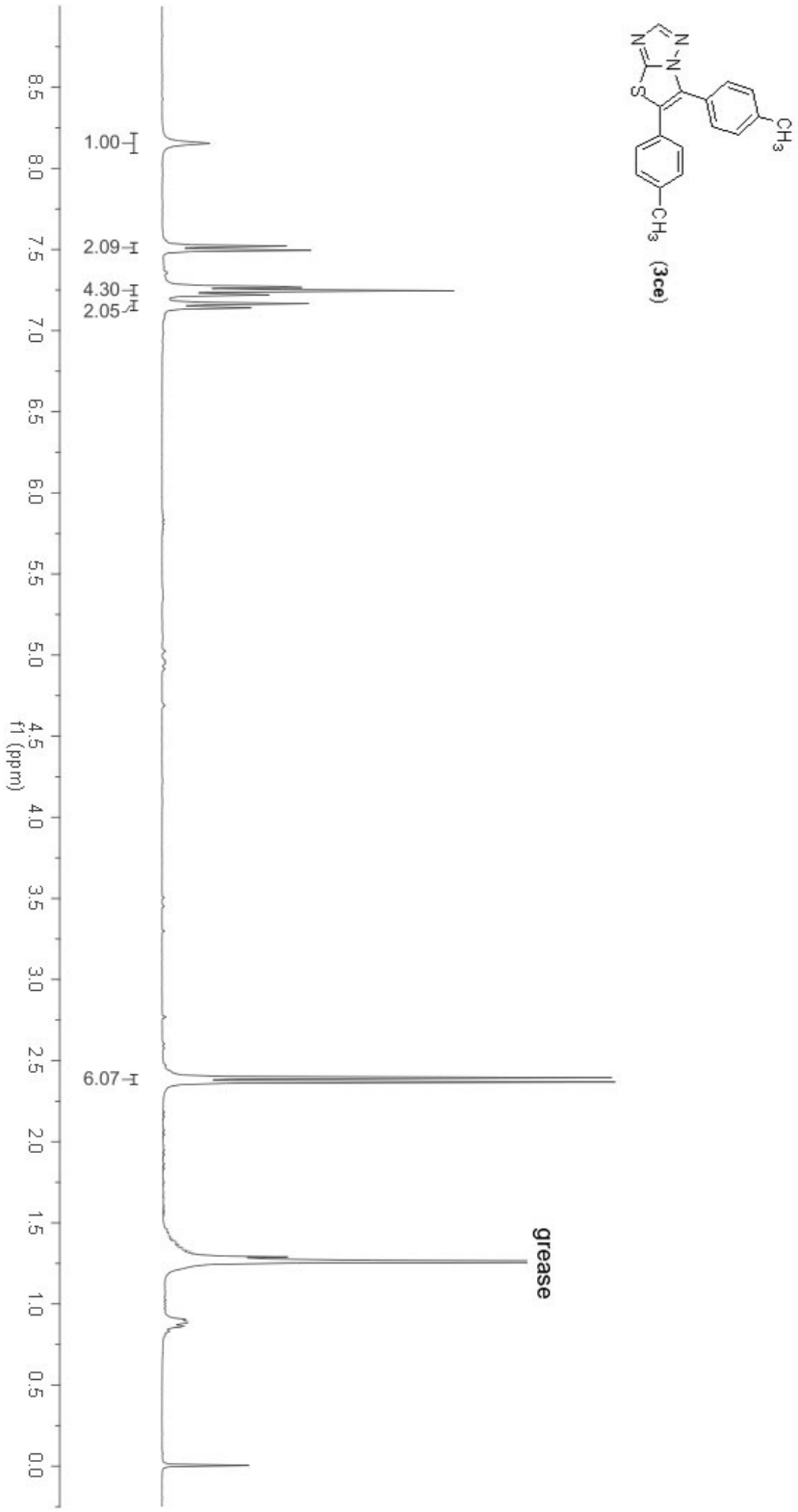
[^{1}H NMR Spectra of **3ce**]



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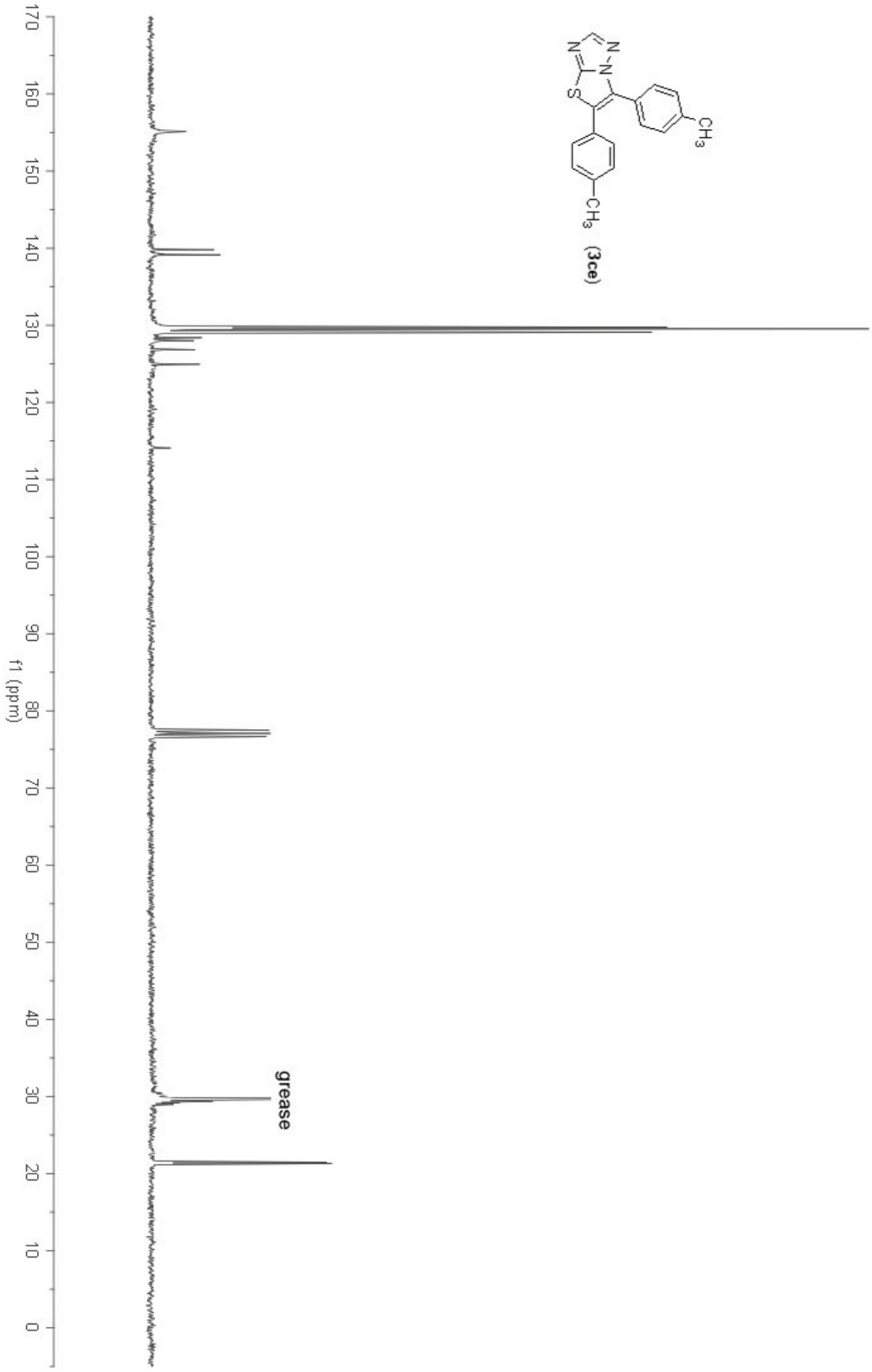

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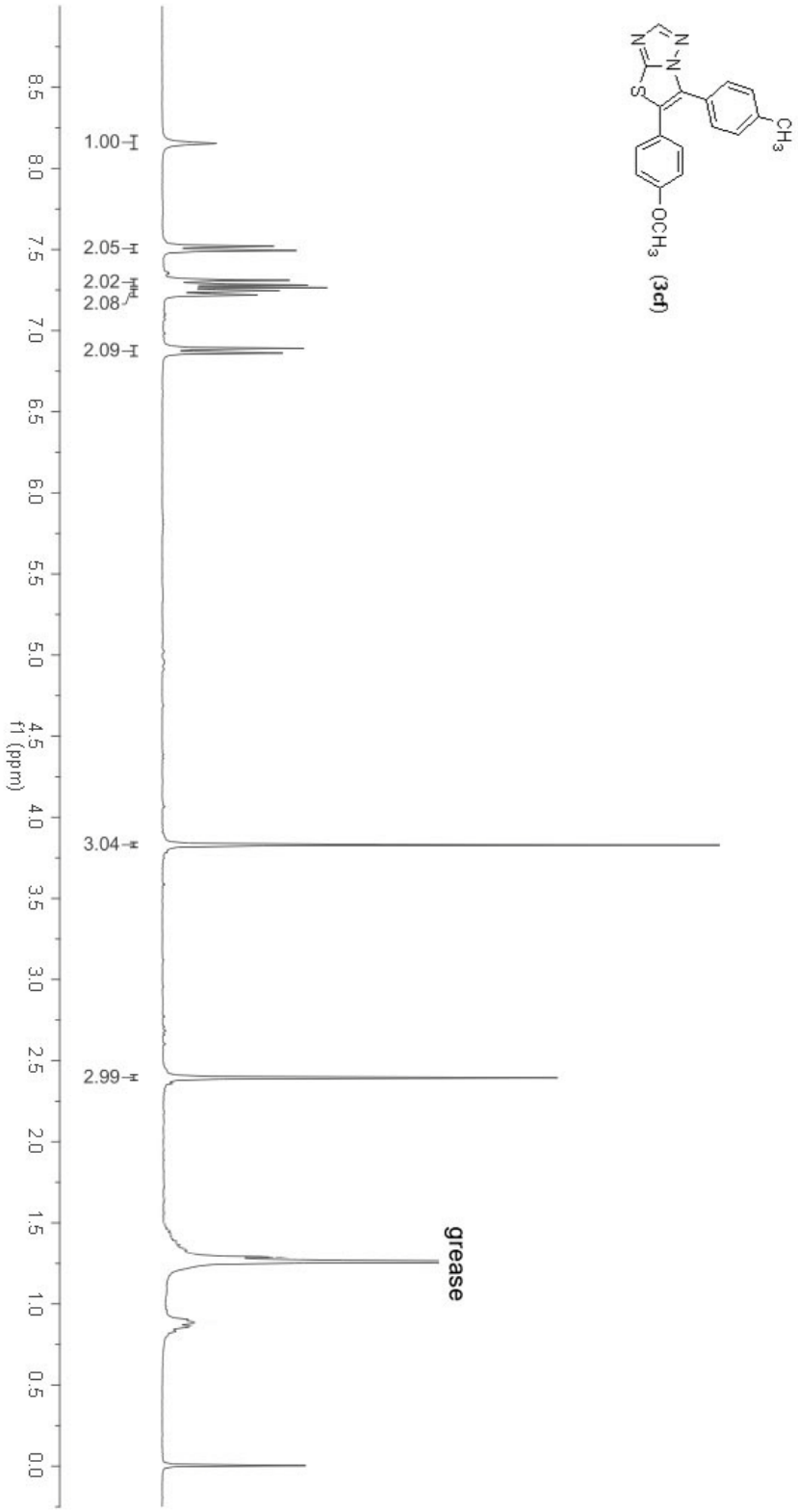
[^{1}H NMR Spectra of **3cf**]



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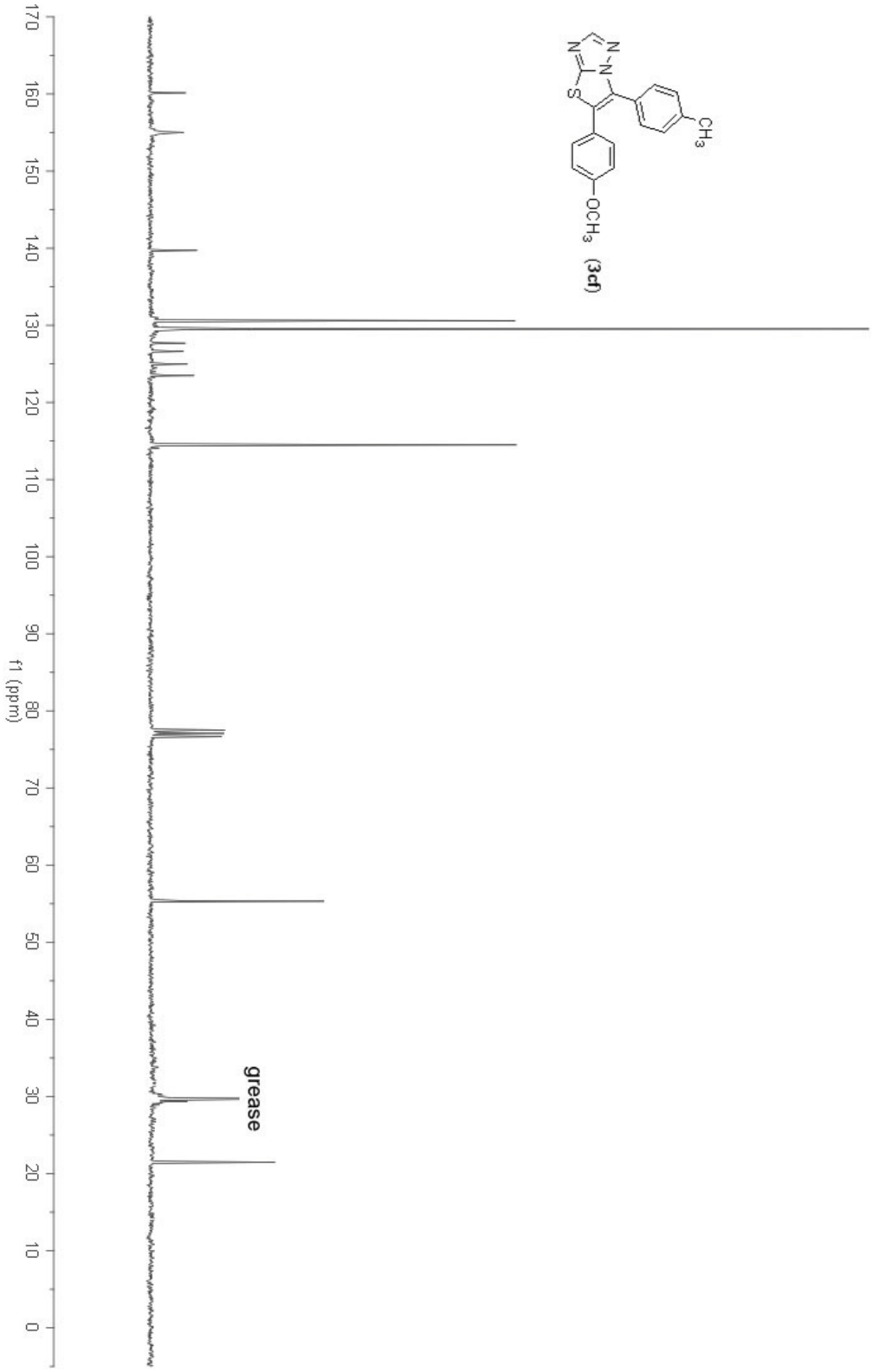

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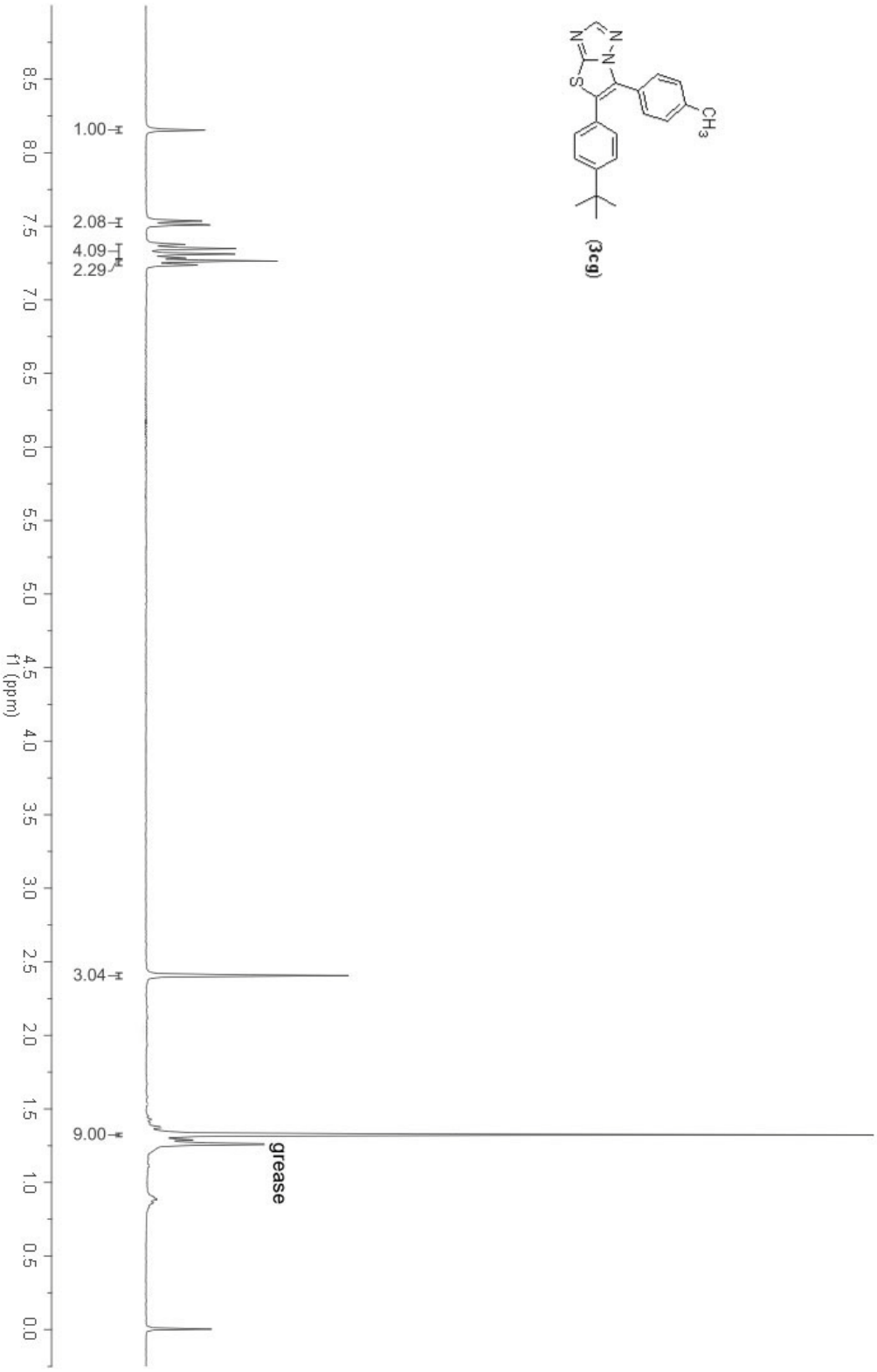
[^{1}H NMR Spectra of **3cg**]



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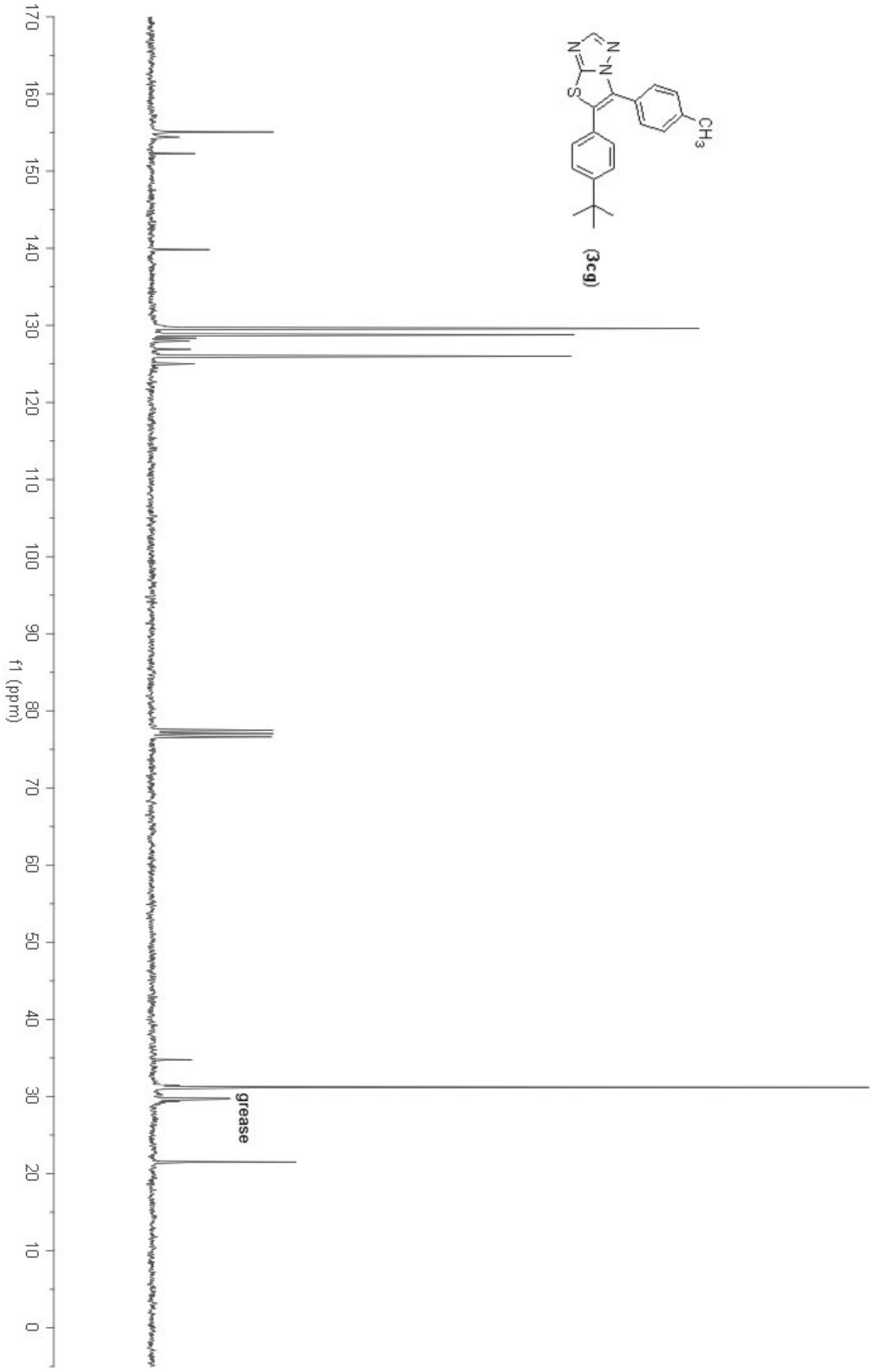

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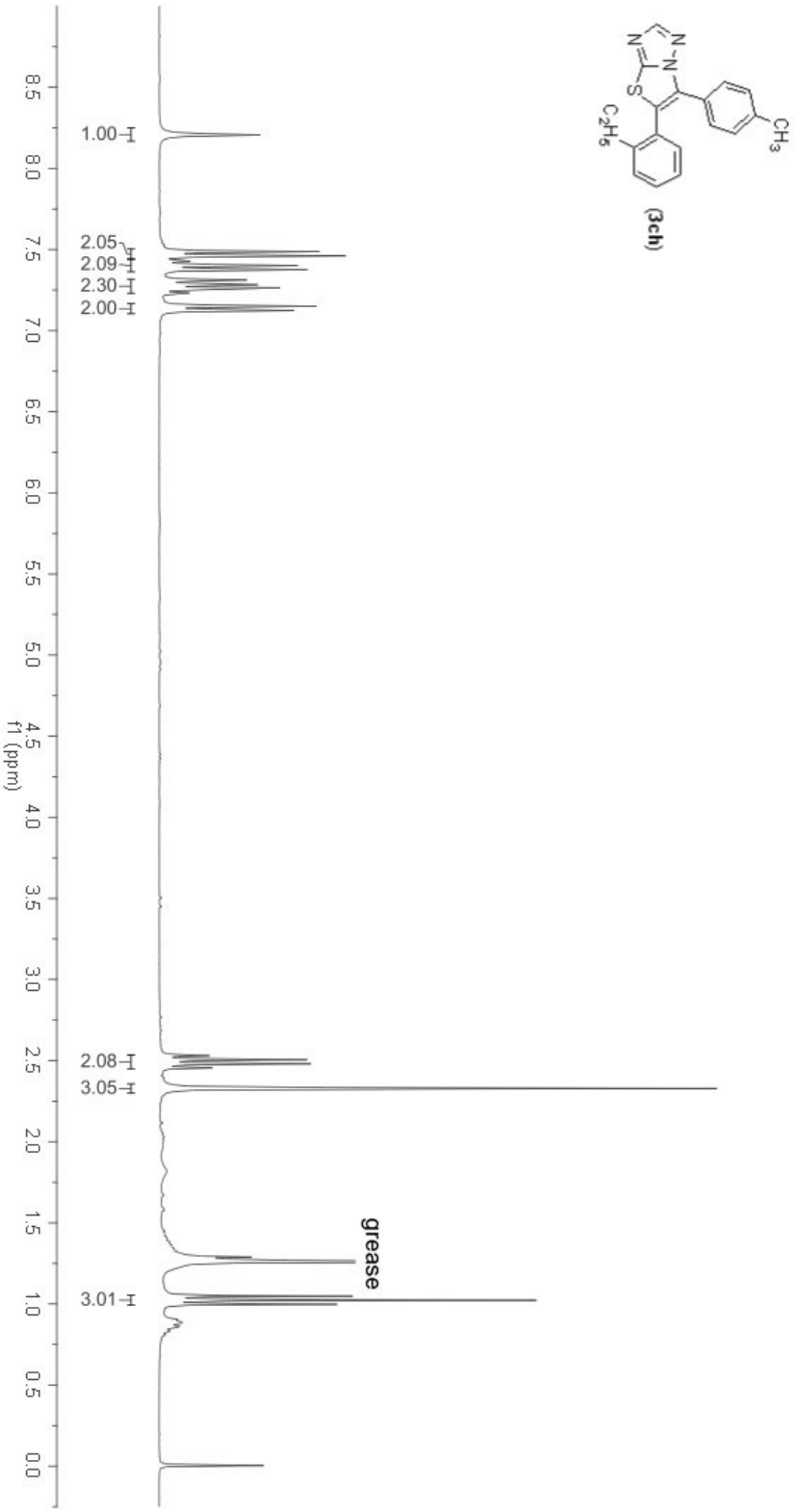
[^{1}H NMR Spectra of **3ch**]



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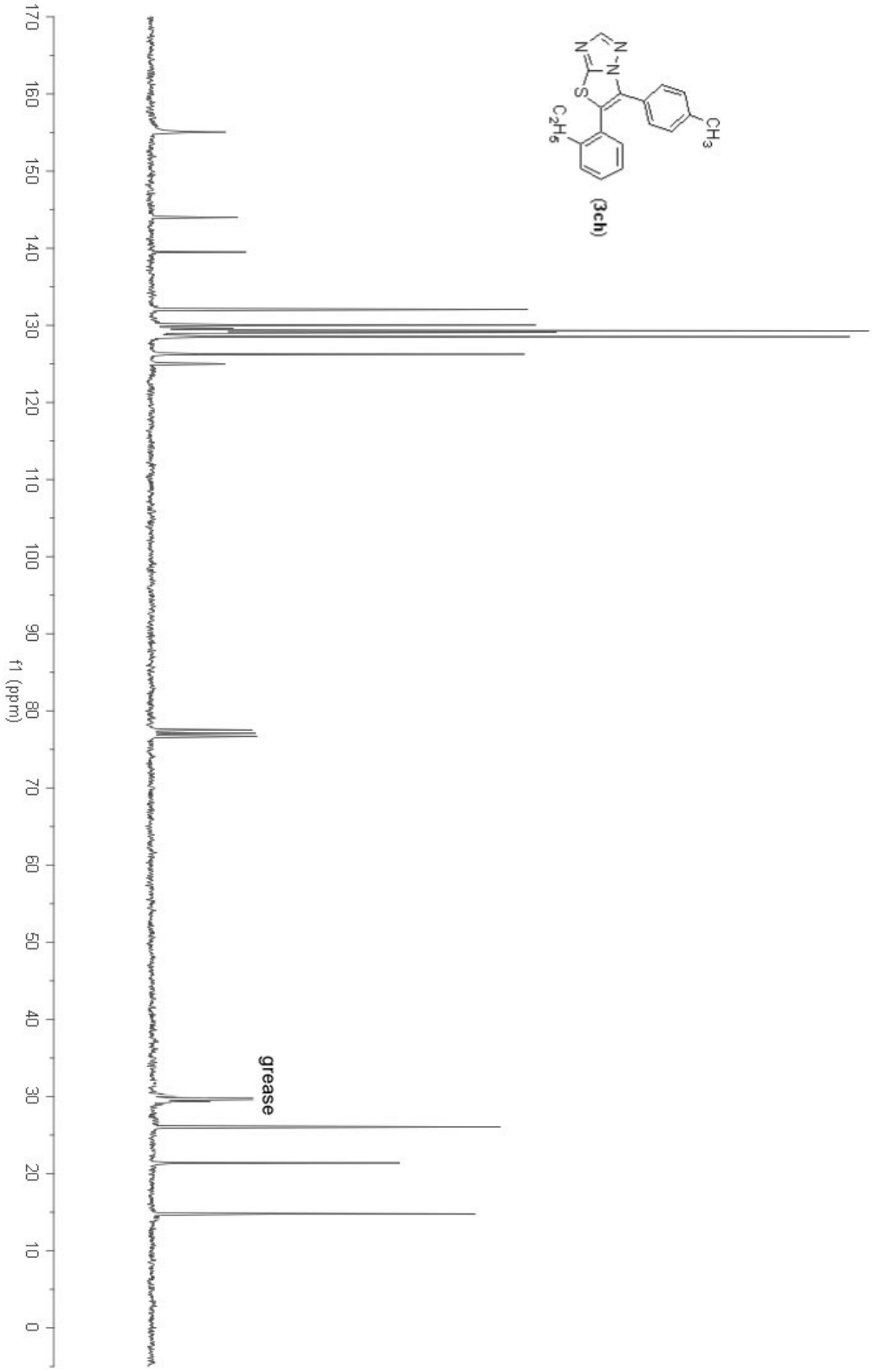

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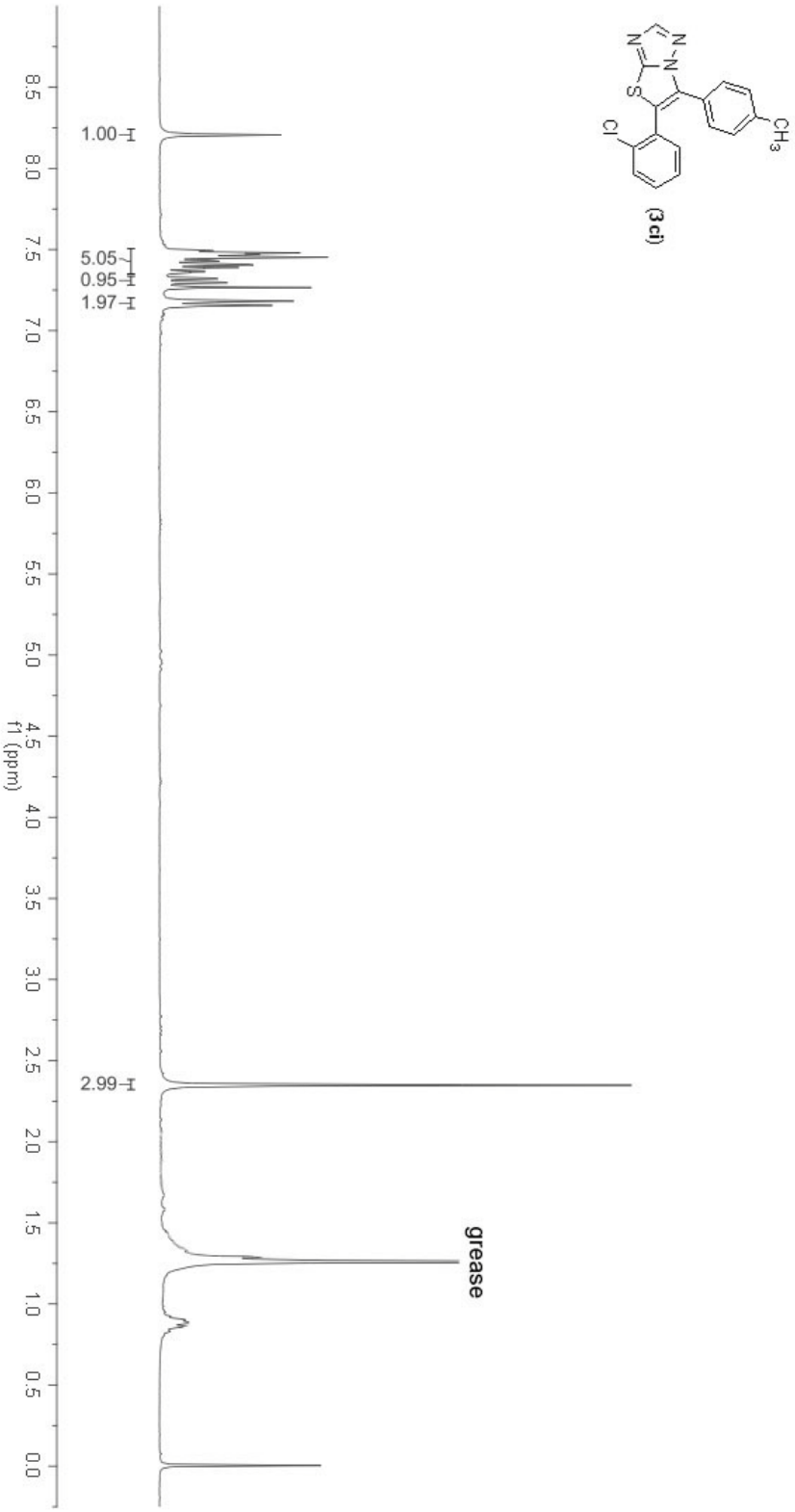
[^{1}H NMR Spectra of **3ci**]



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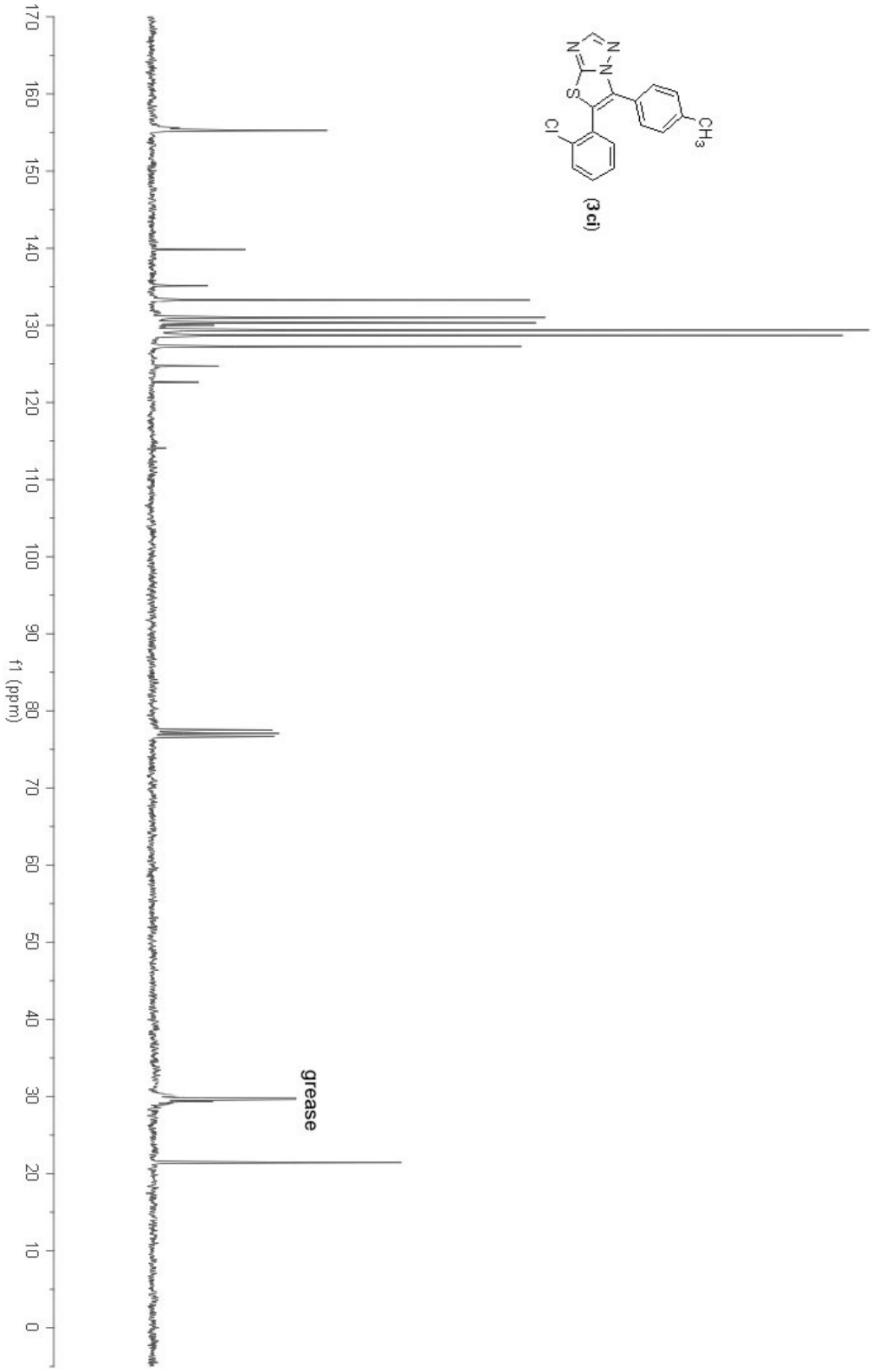

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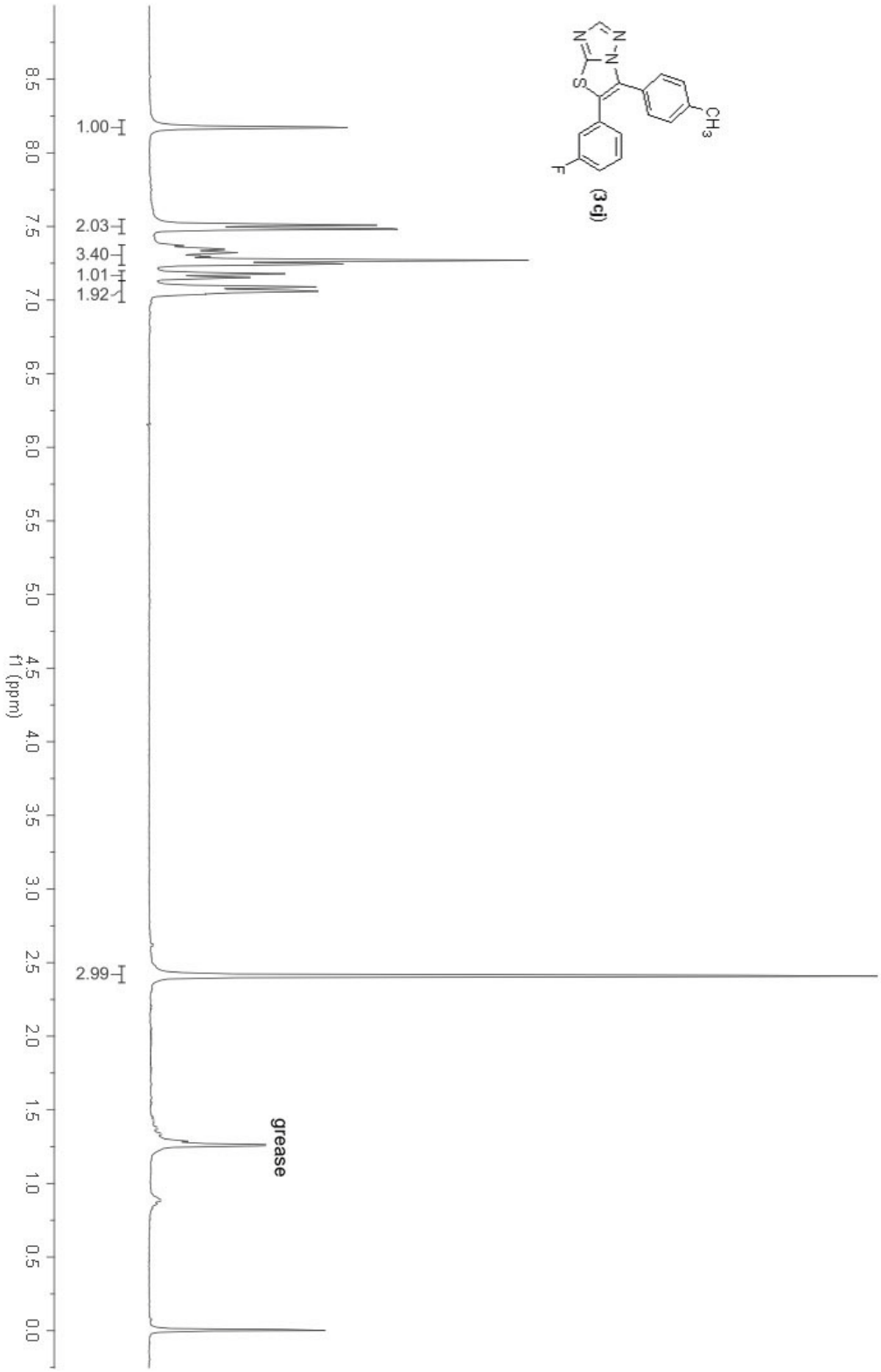

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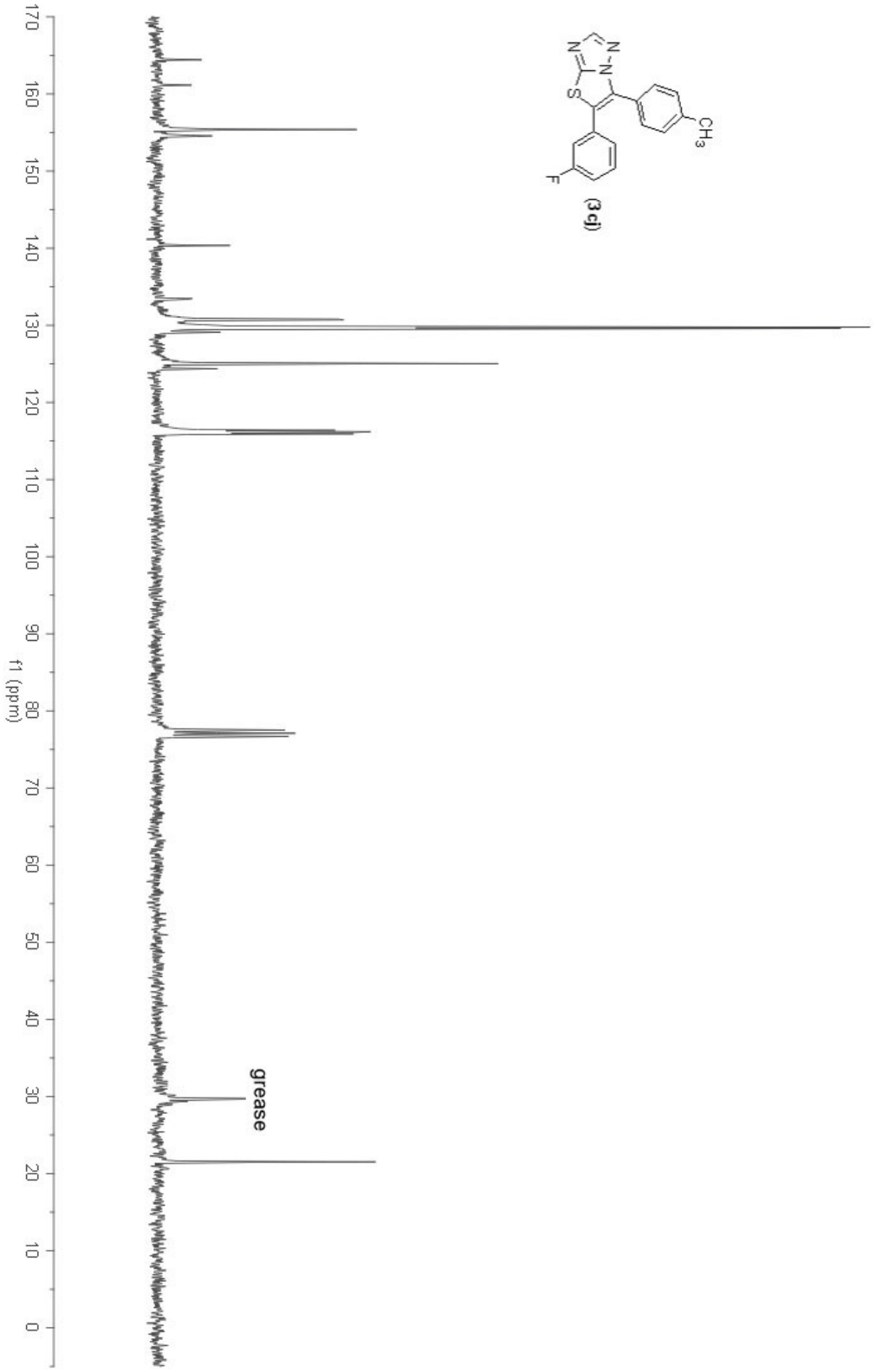

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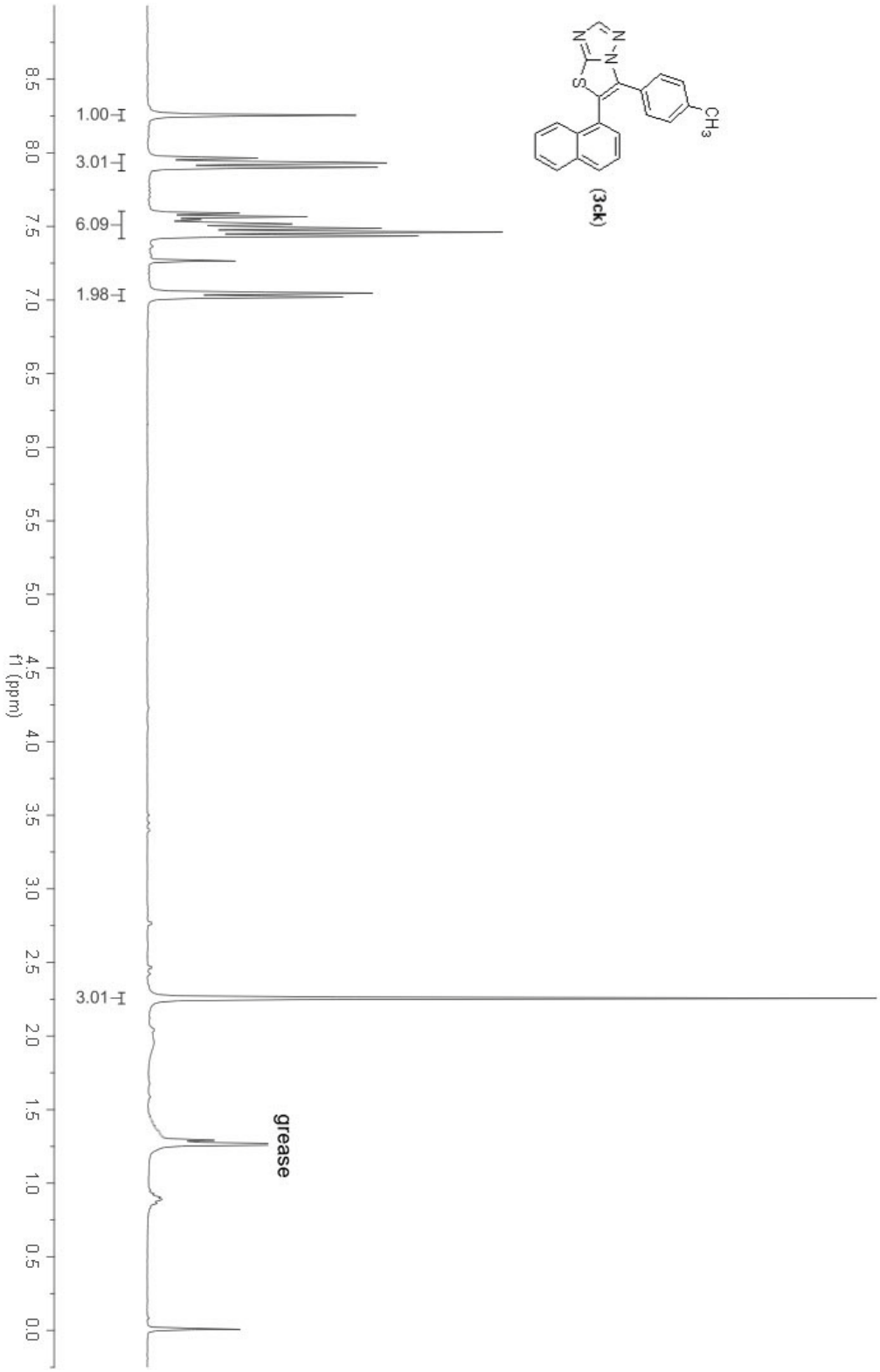
[^{1}H NMR Spectra of **3ck**]



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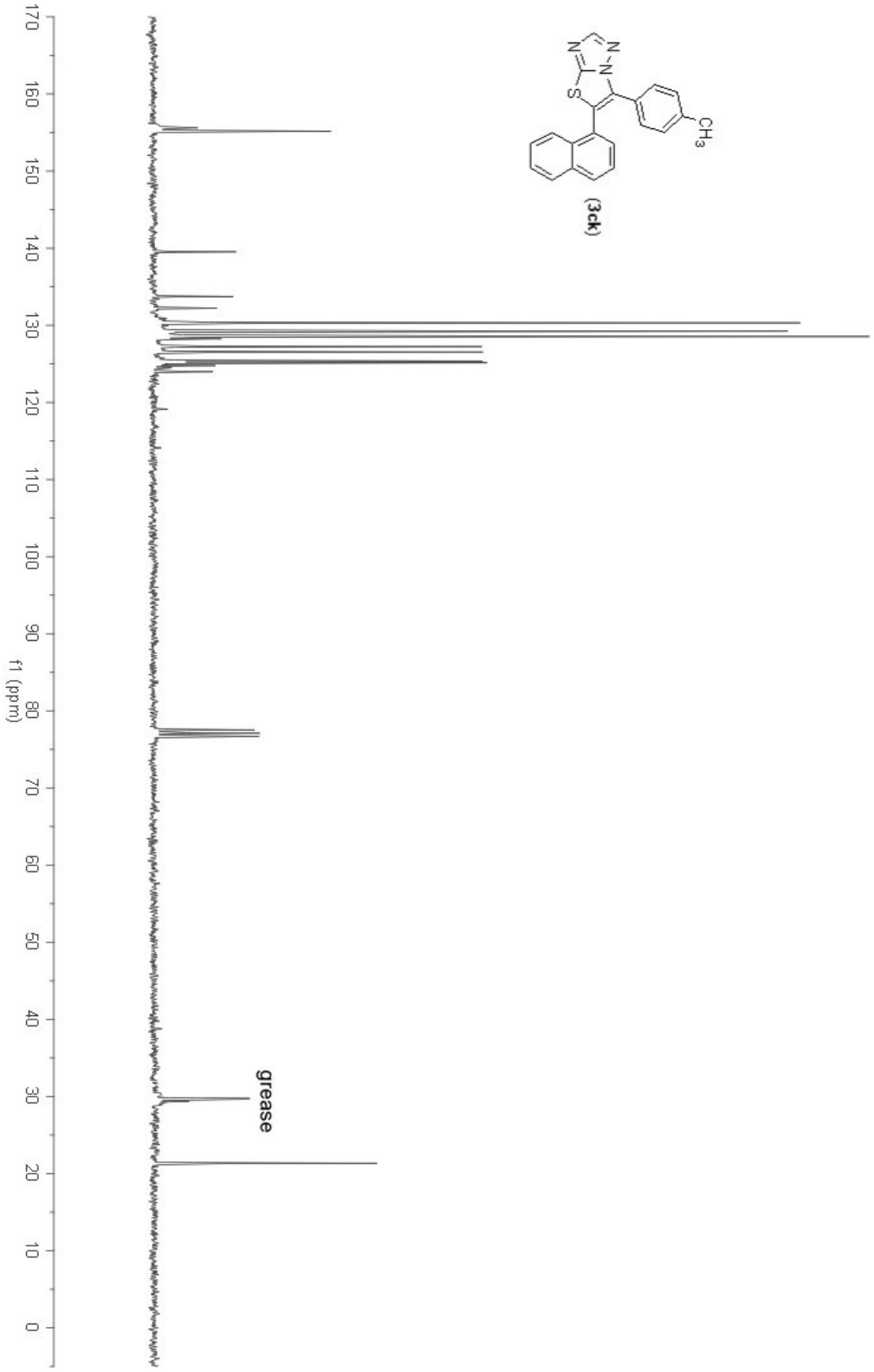

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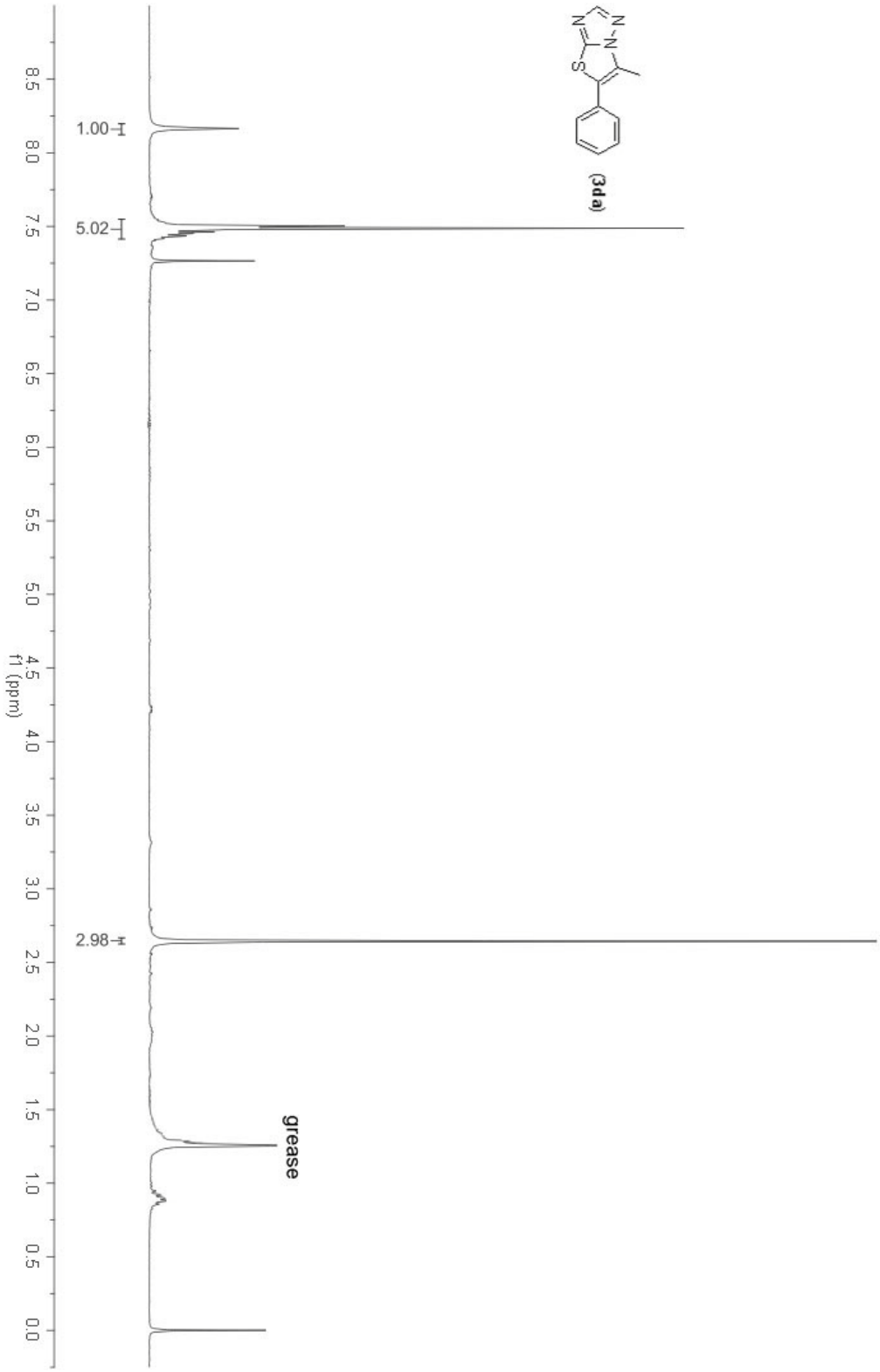
[^{1}H NMR Spectra of **3da**]



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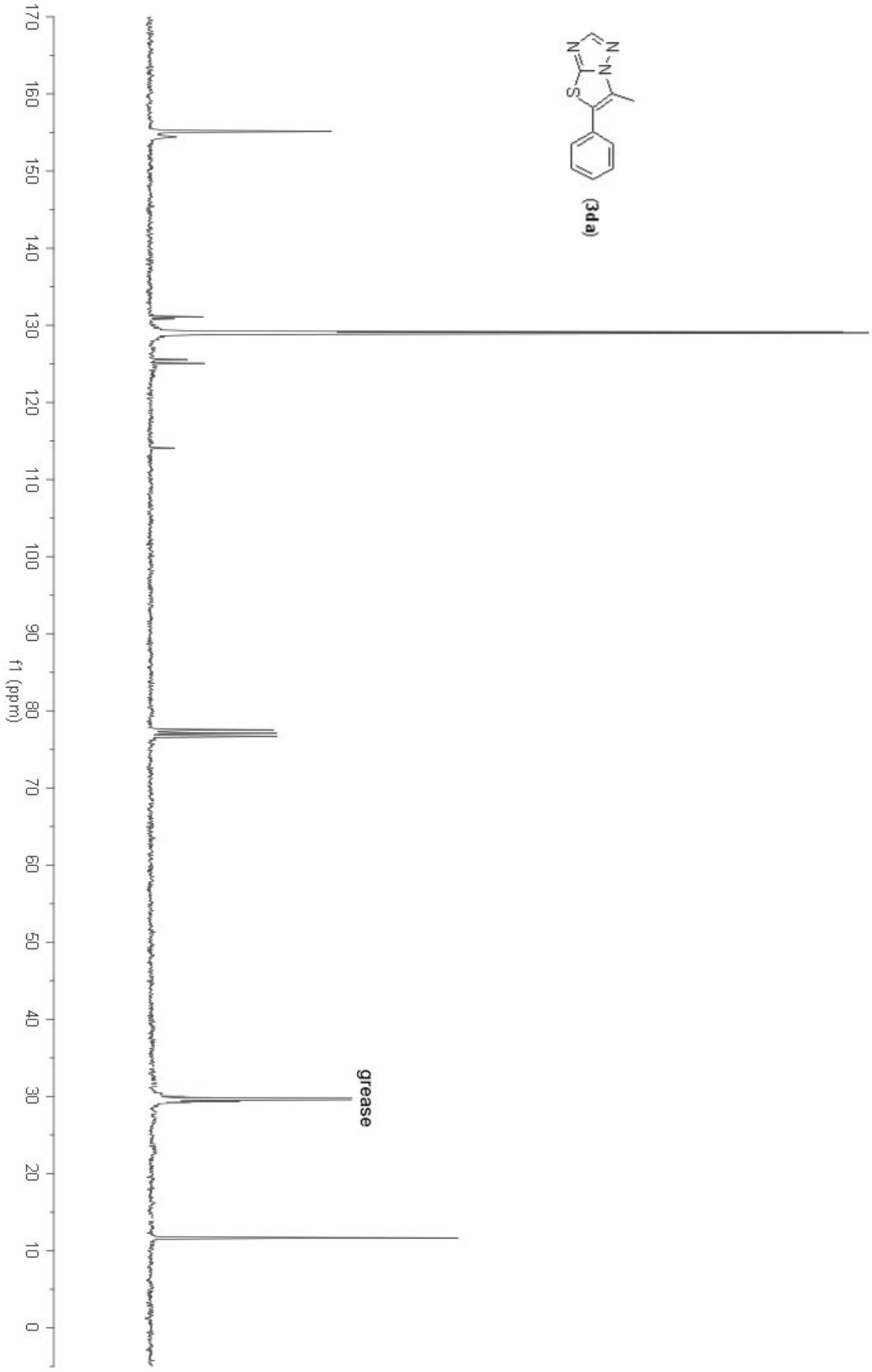

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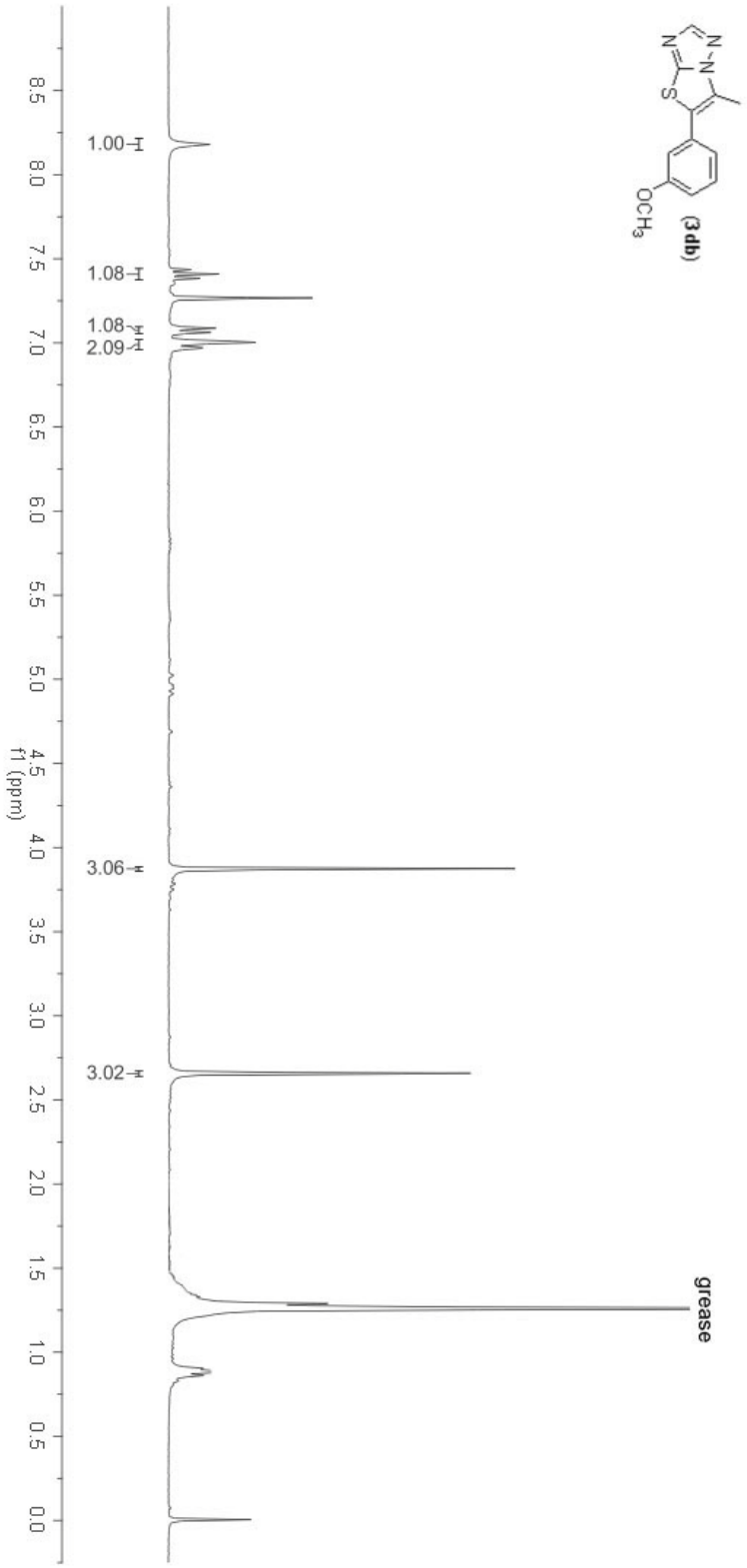

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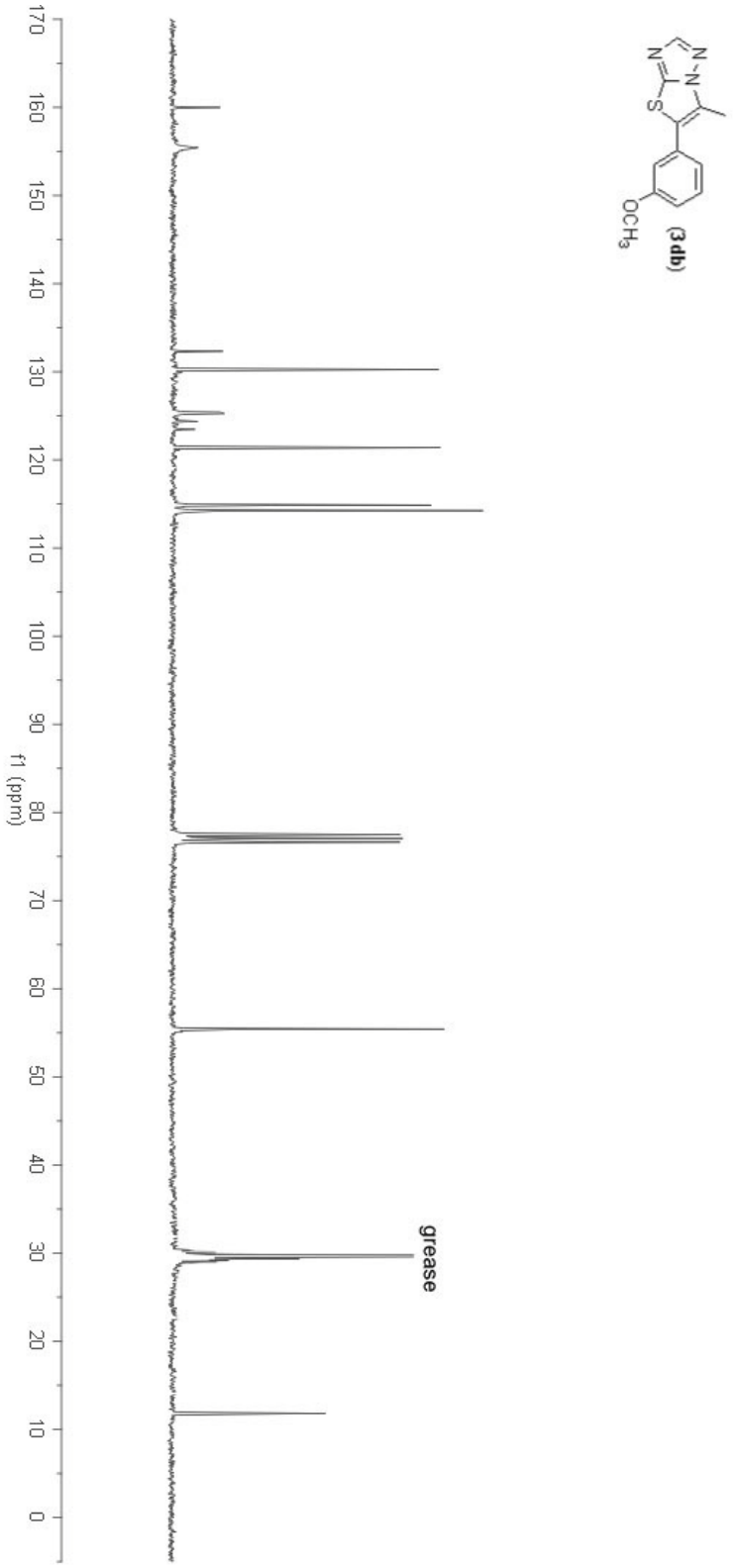

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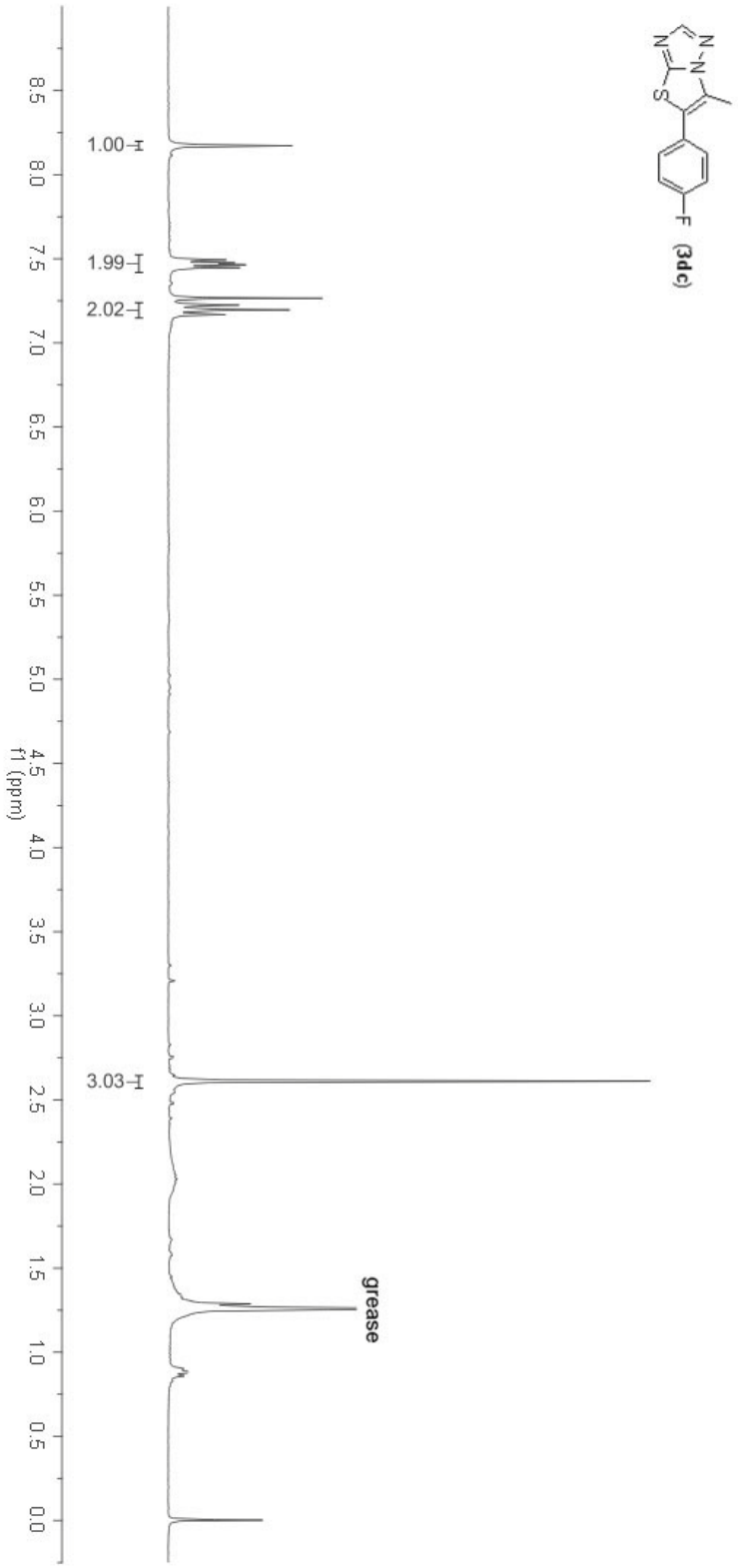
[^{1}H NMR Spectra of **3dc**]



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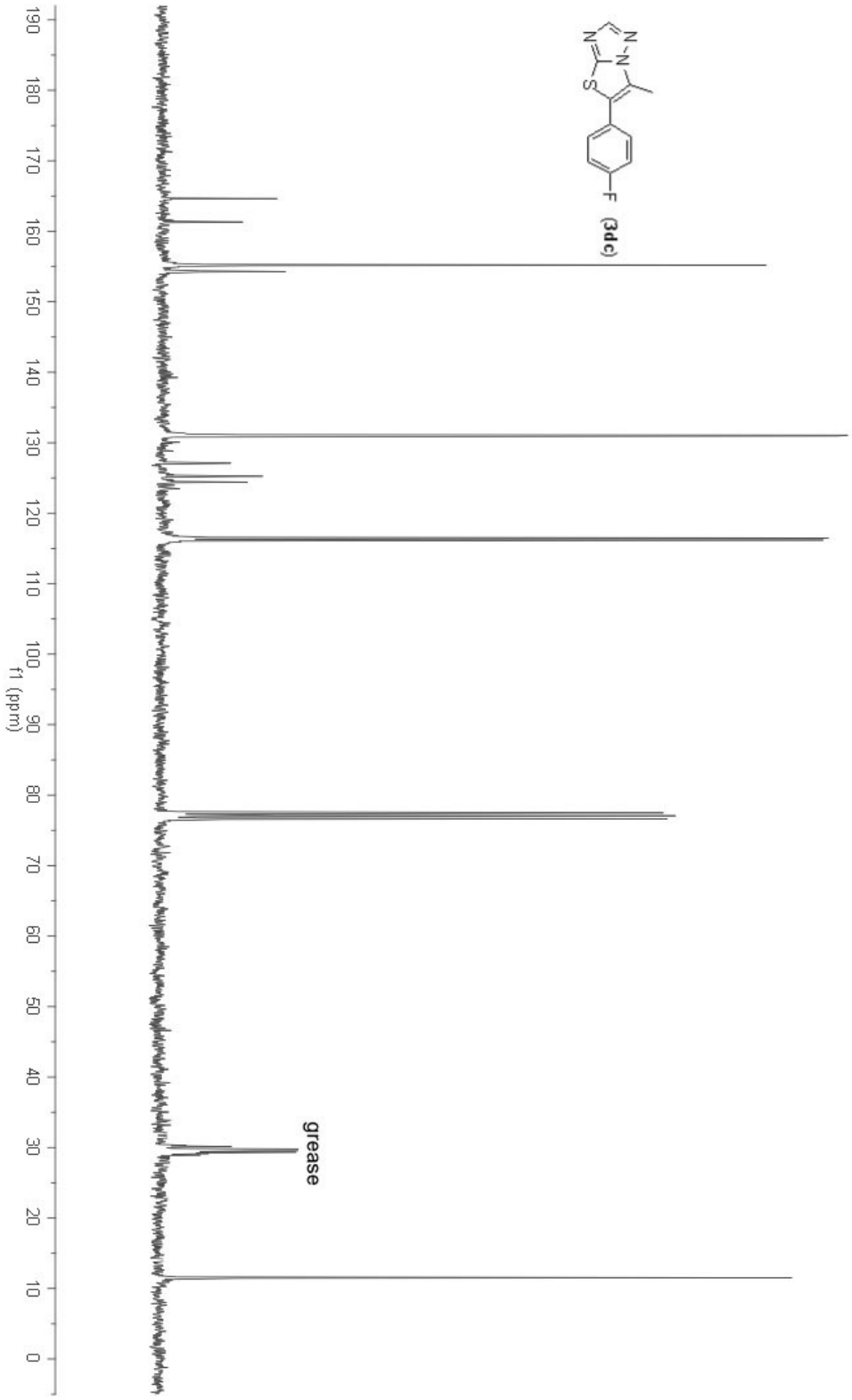

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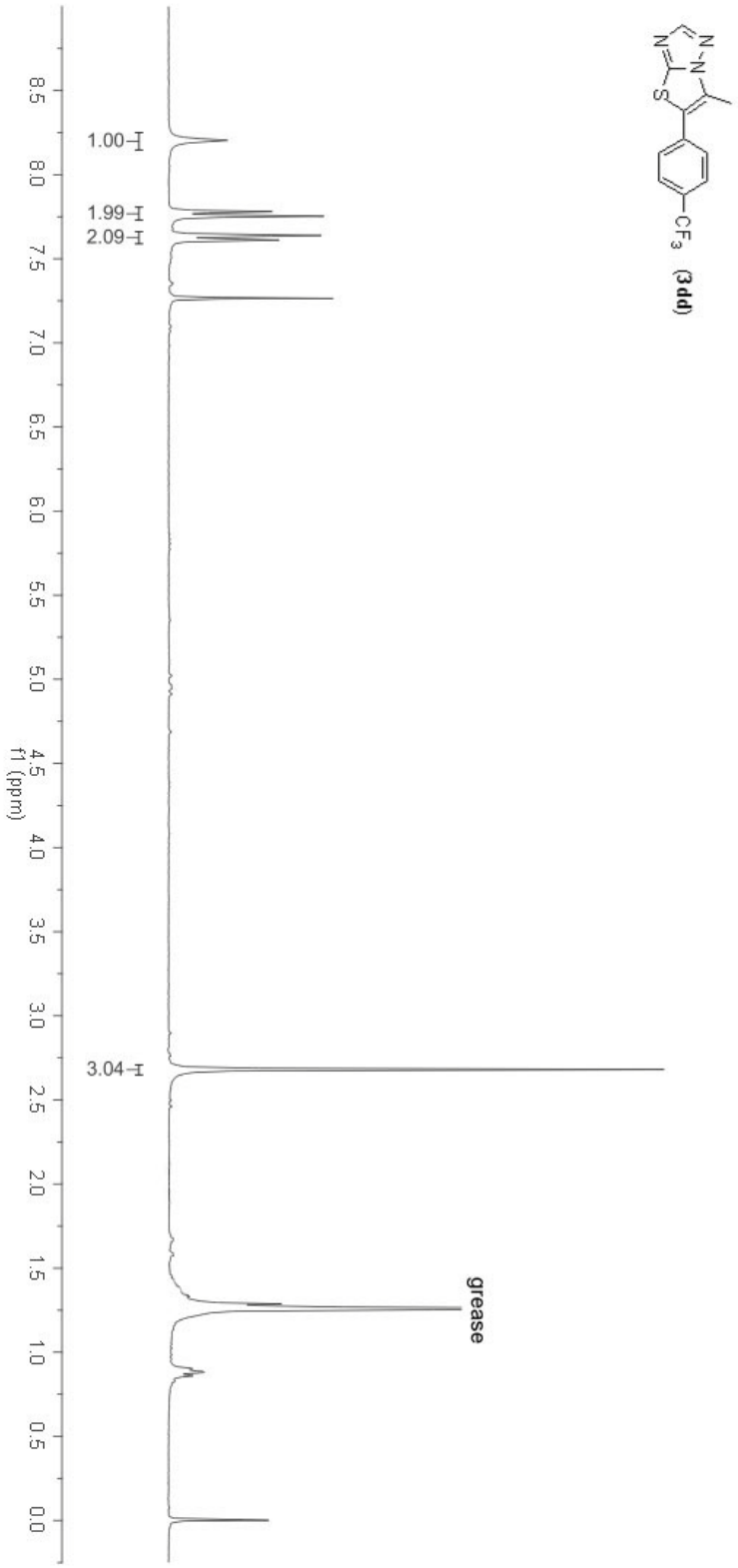
[^{1}H NMR Spectra of **3dd**]



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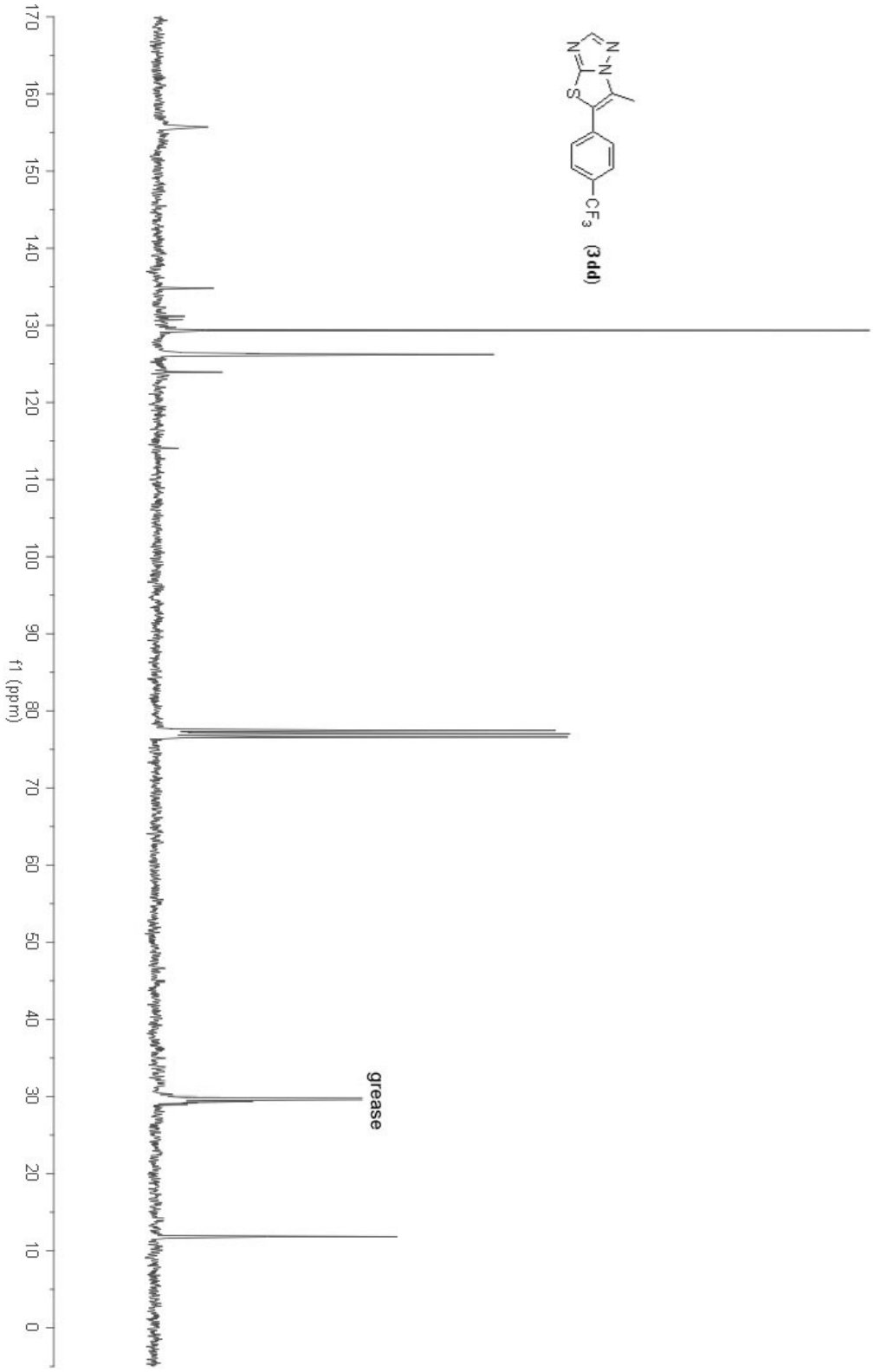

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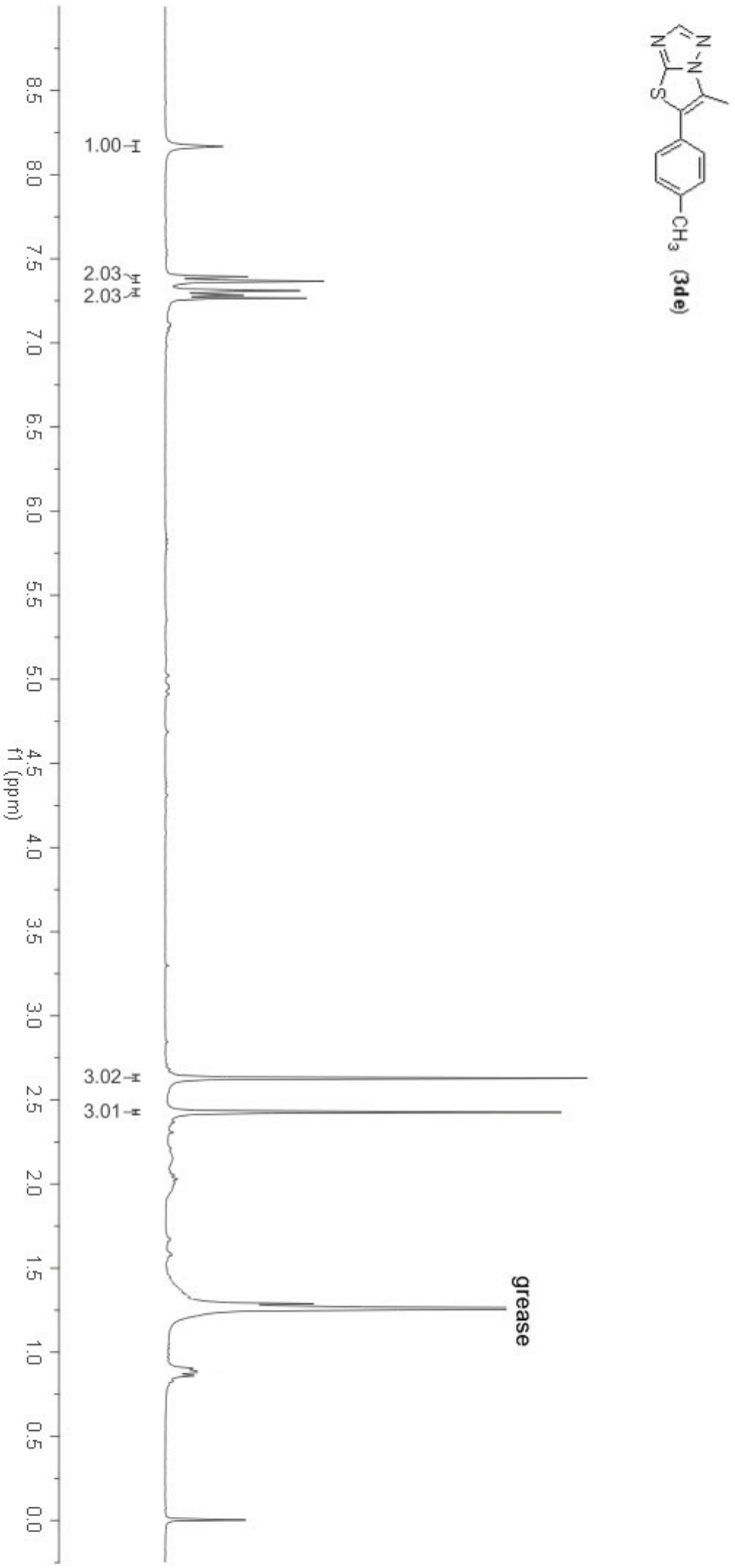
[^{1}H NMR Spectra of **3de**]



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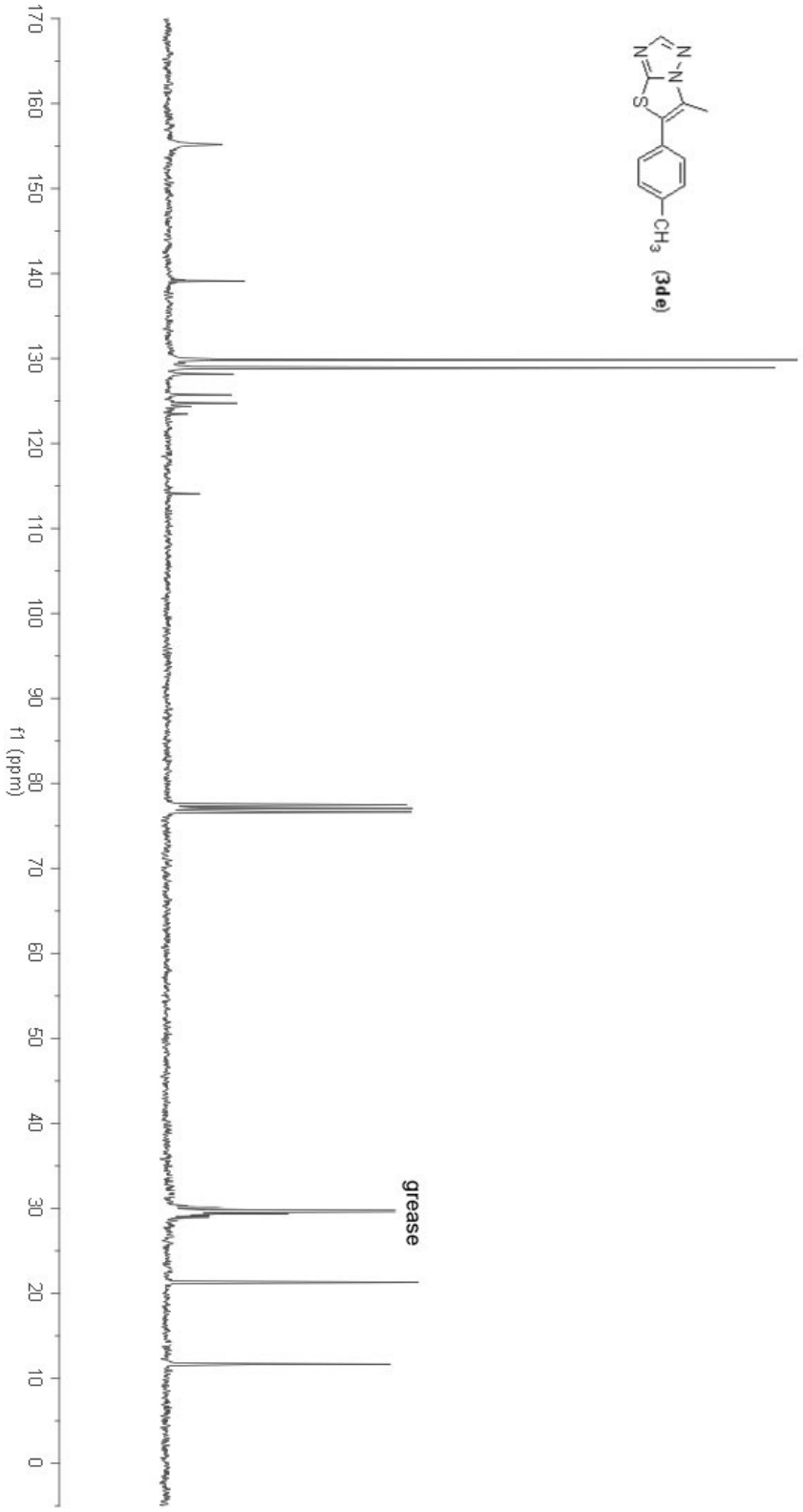

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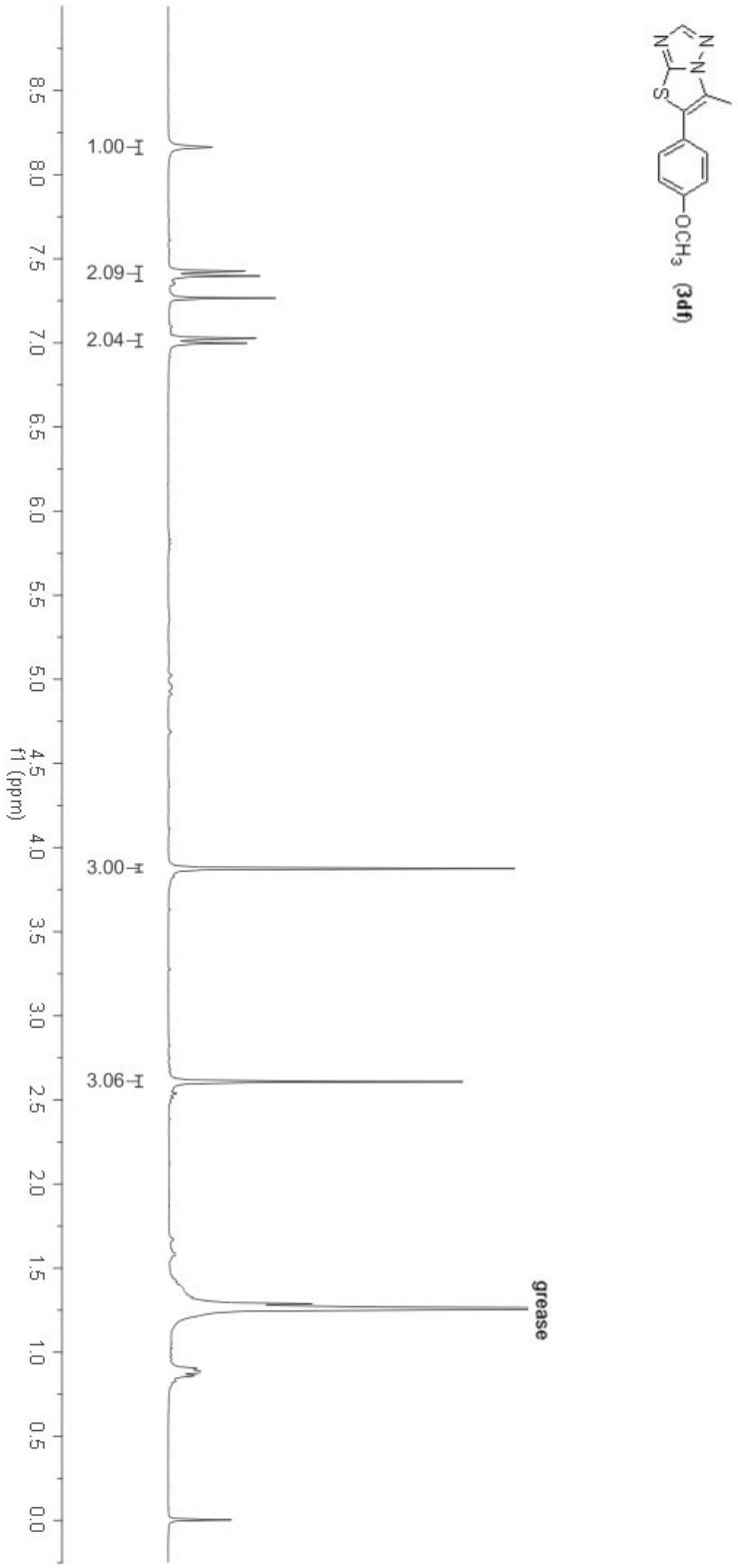

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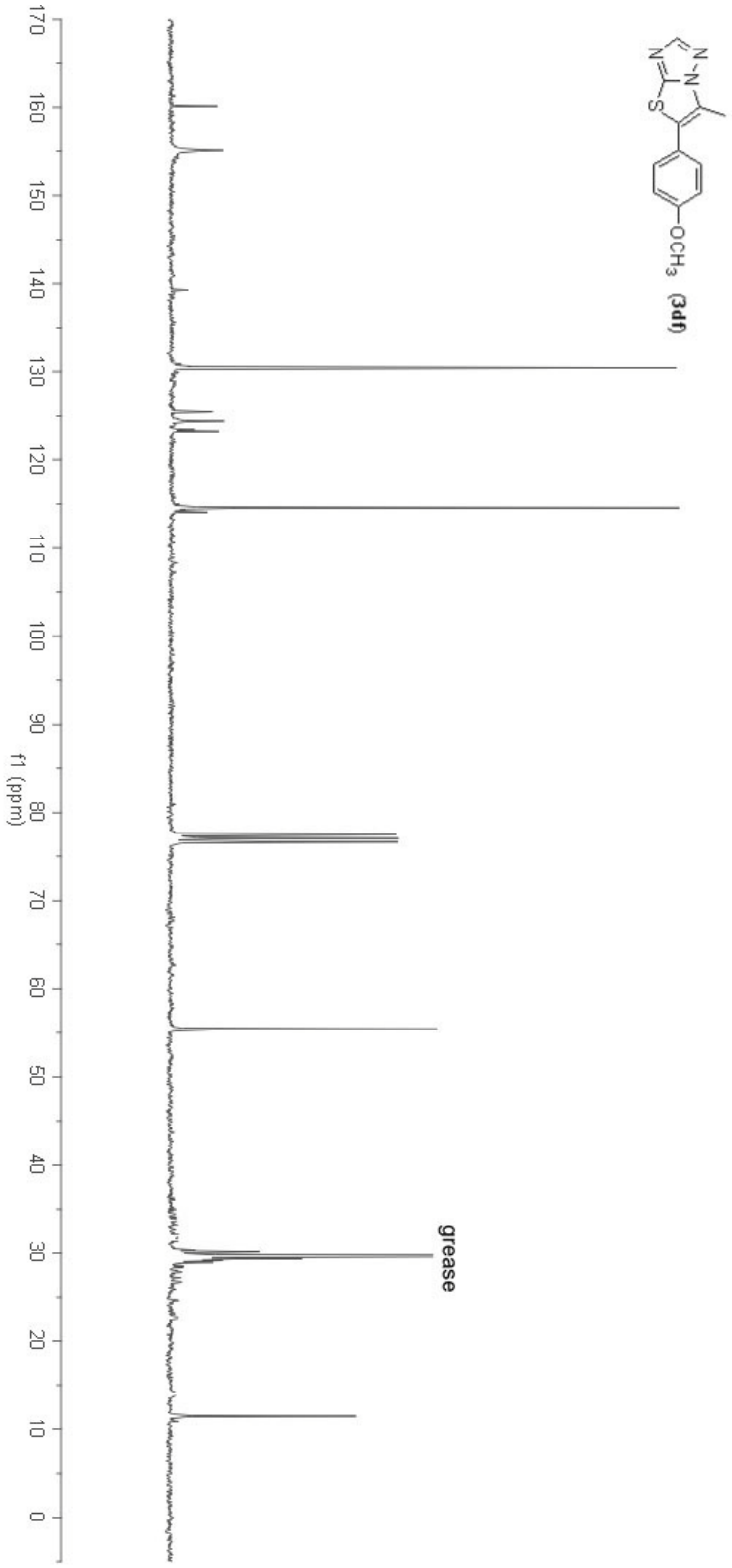

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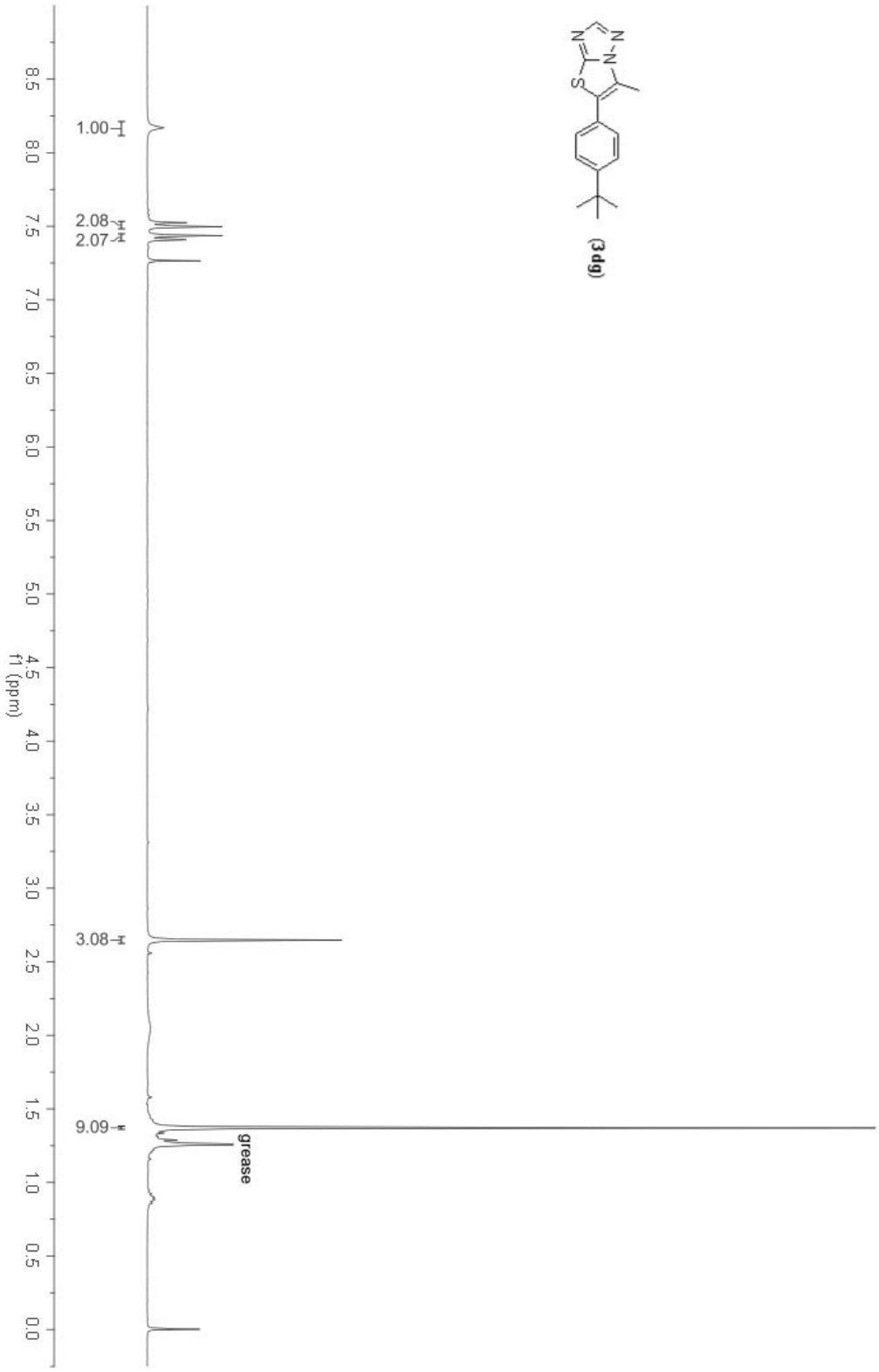
[^{1}H NMR Spectra of **3dg**]



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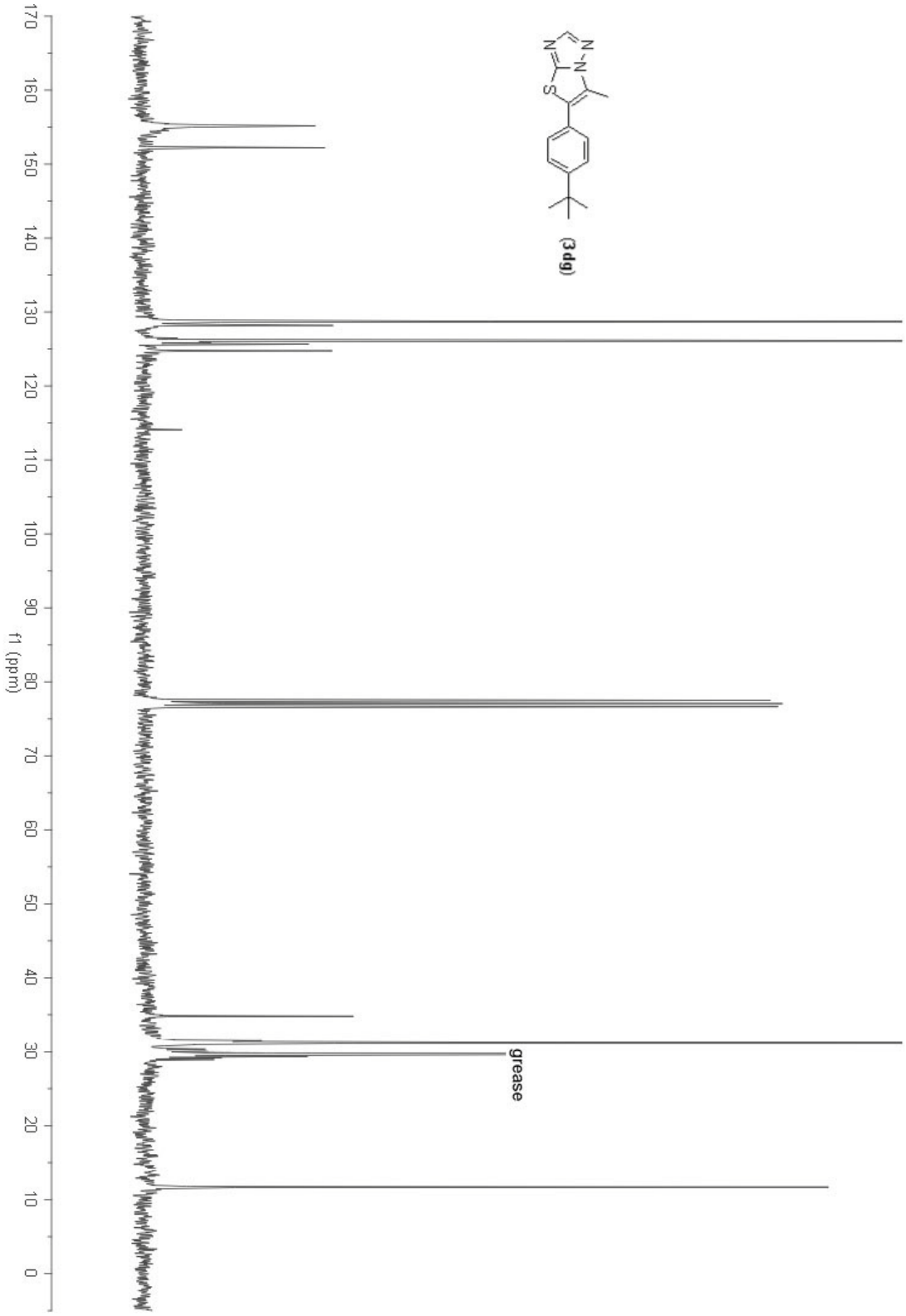

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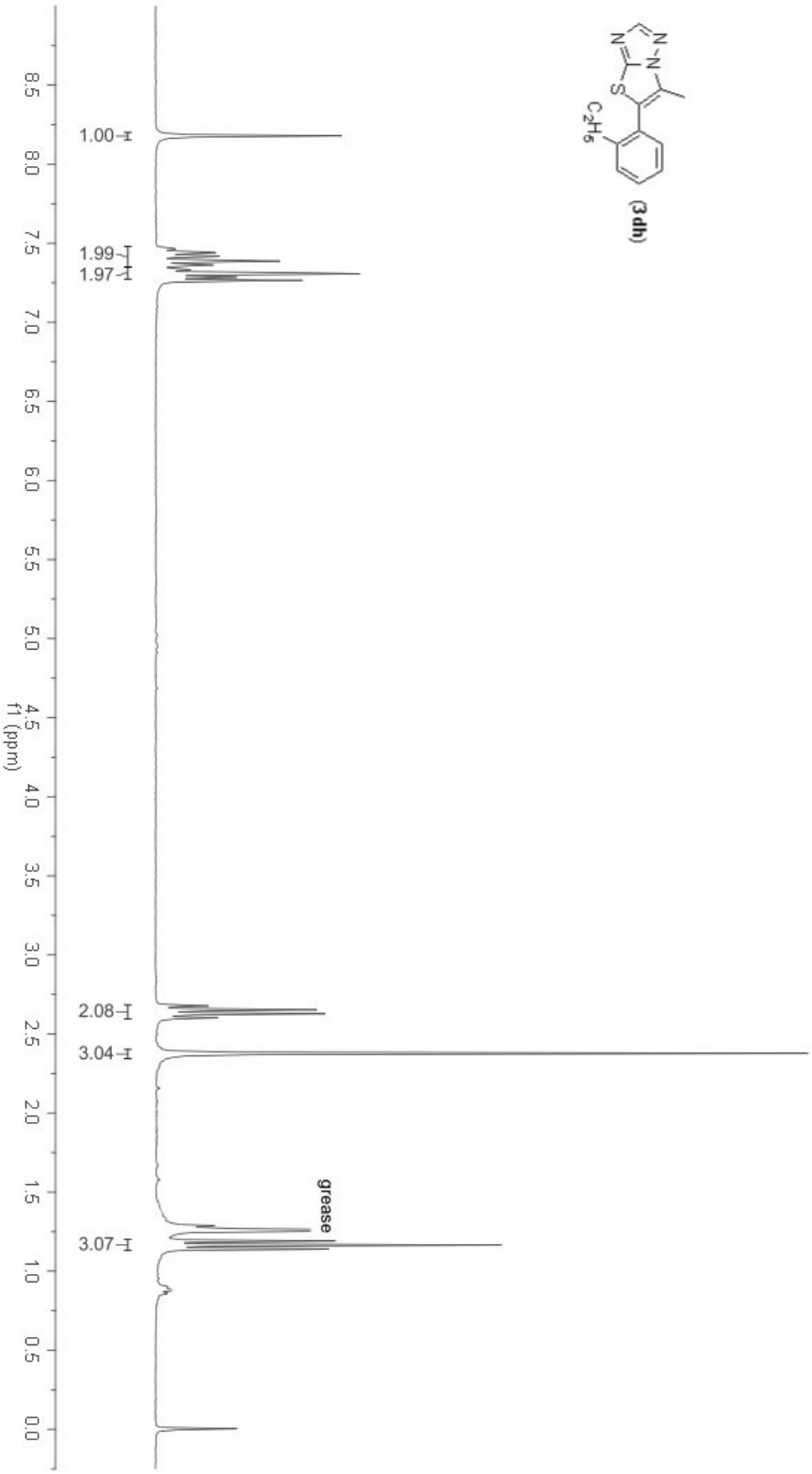
[^{1}H NMR Spectra of **3dh**]



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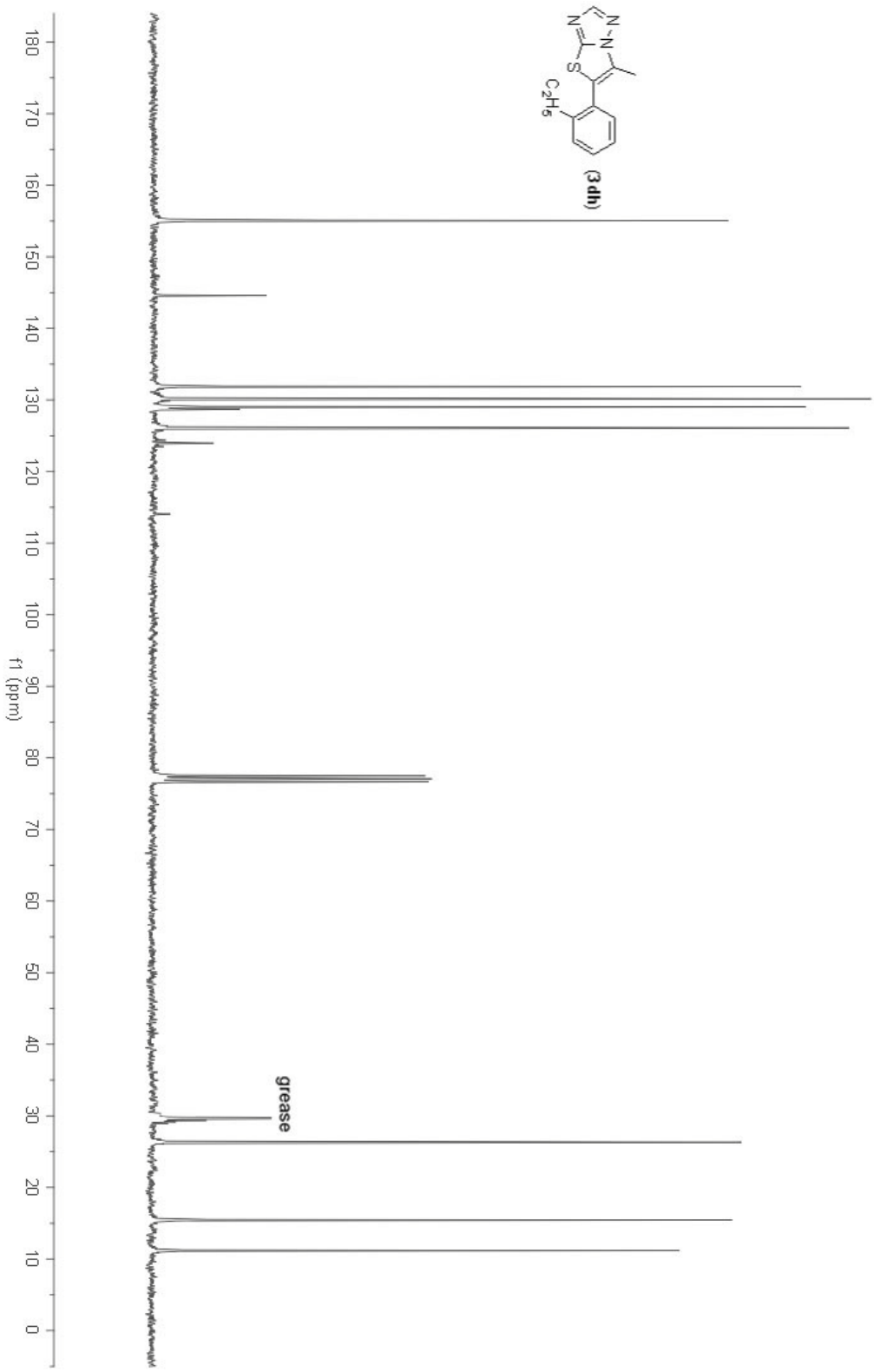
[^{13}C NMR Spectra of **3dh**]



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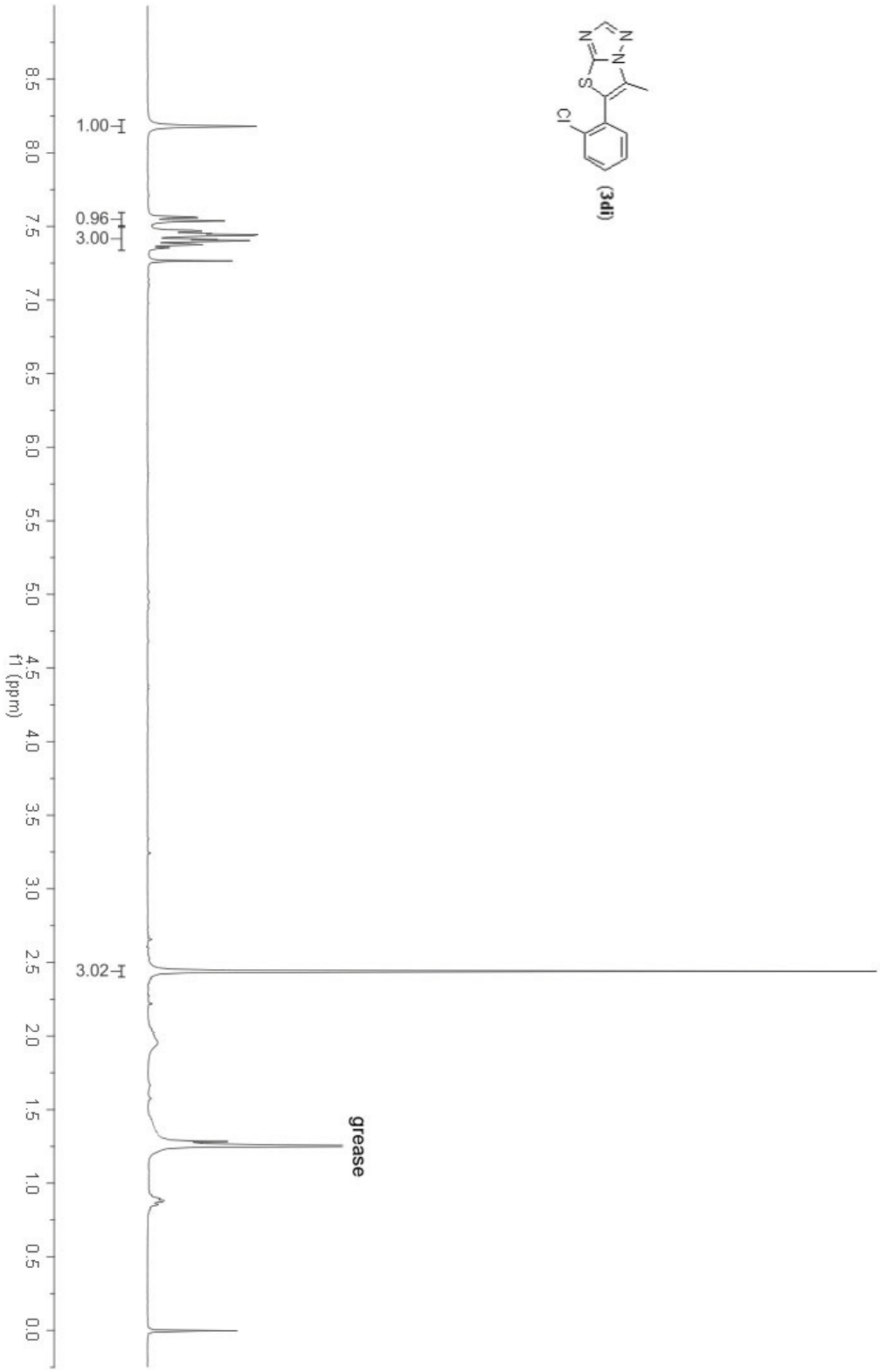

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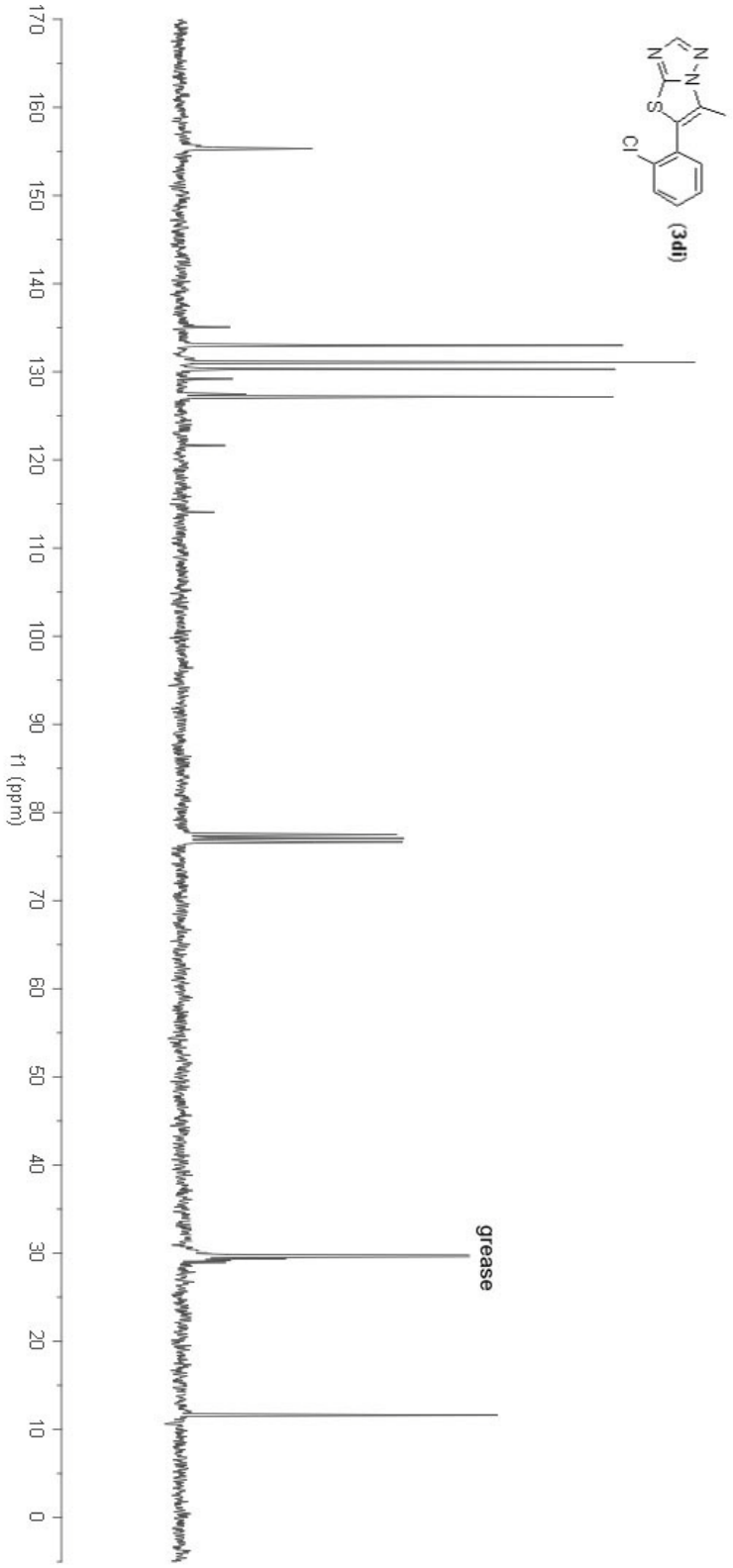
[^{13}C NMR Spectra of **3di**]



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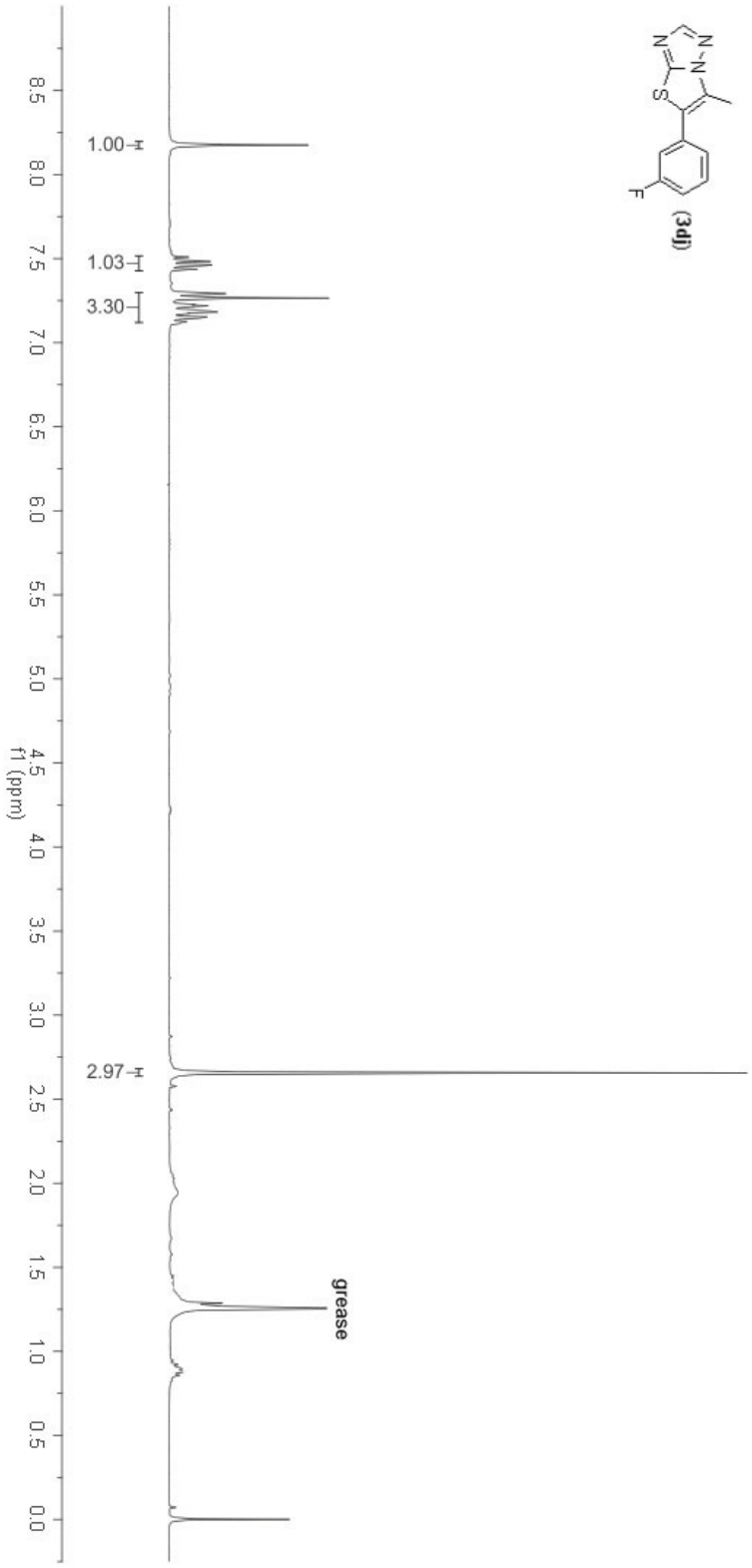

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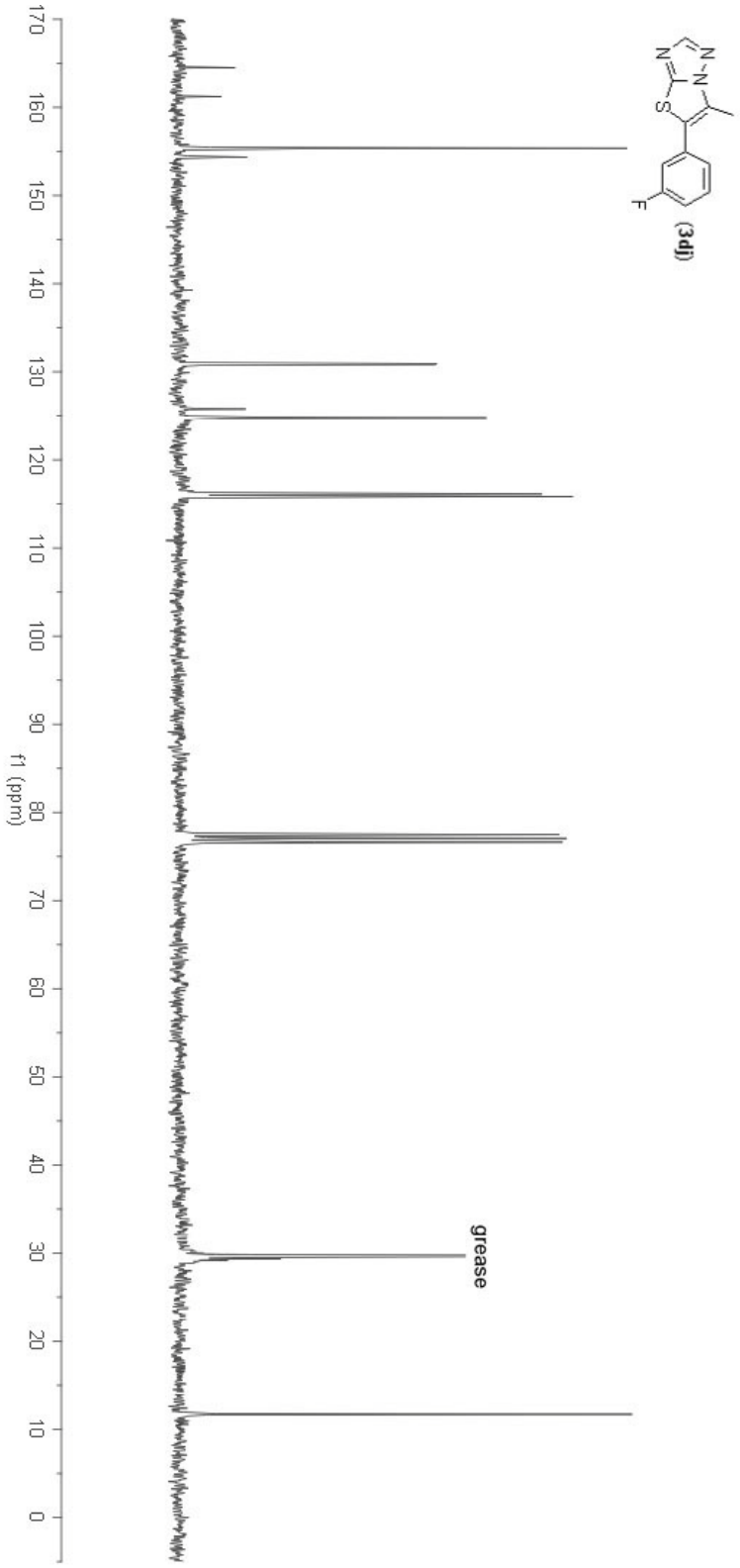
[^{13}C NMR Spectra of **3dj**]



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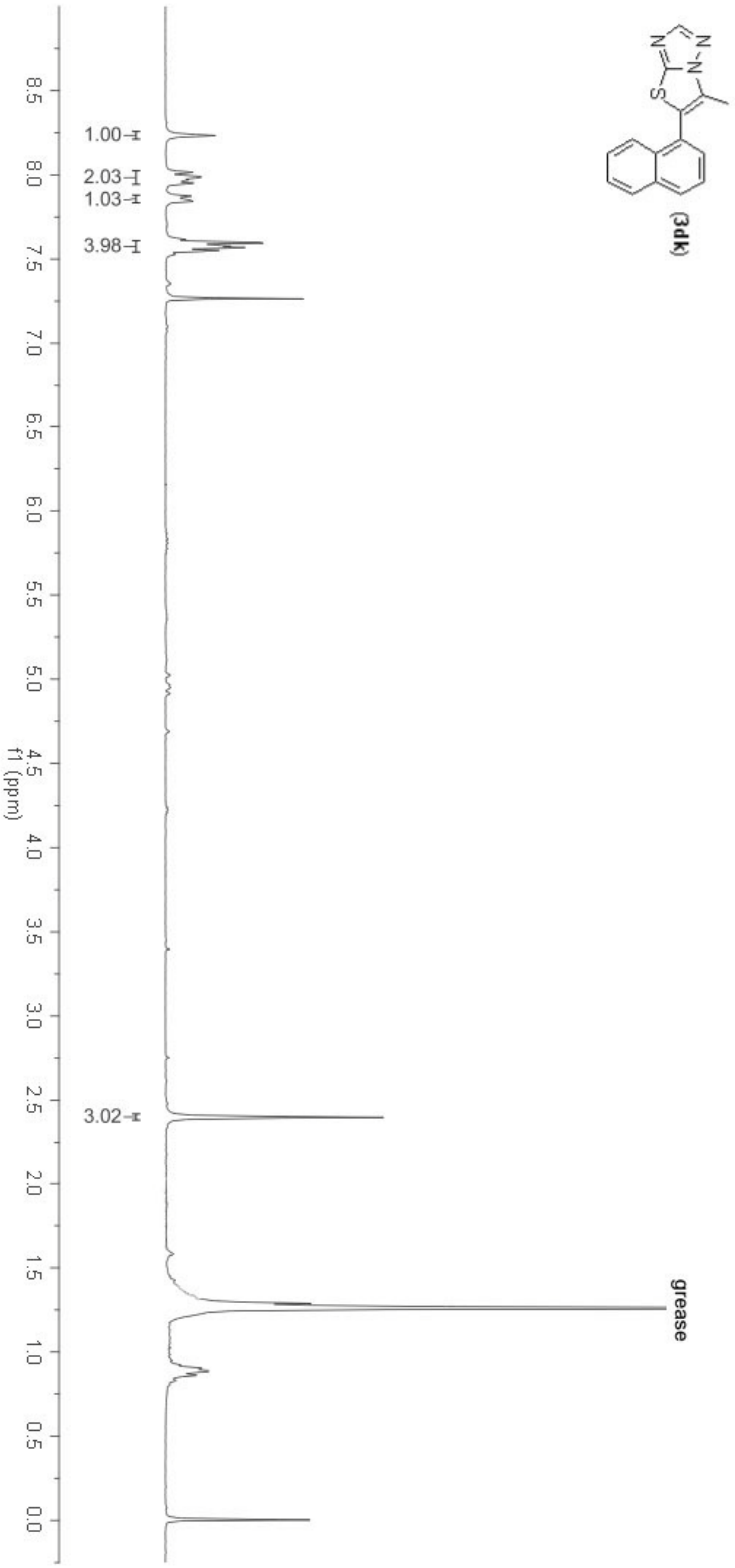
[^{1}H NMR Spectra of **3dk**]



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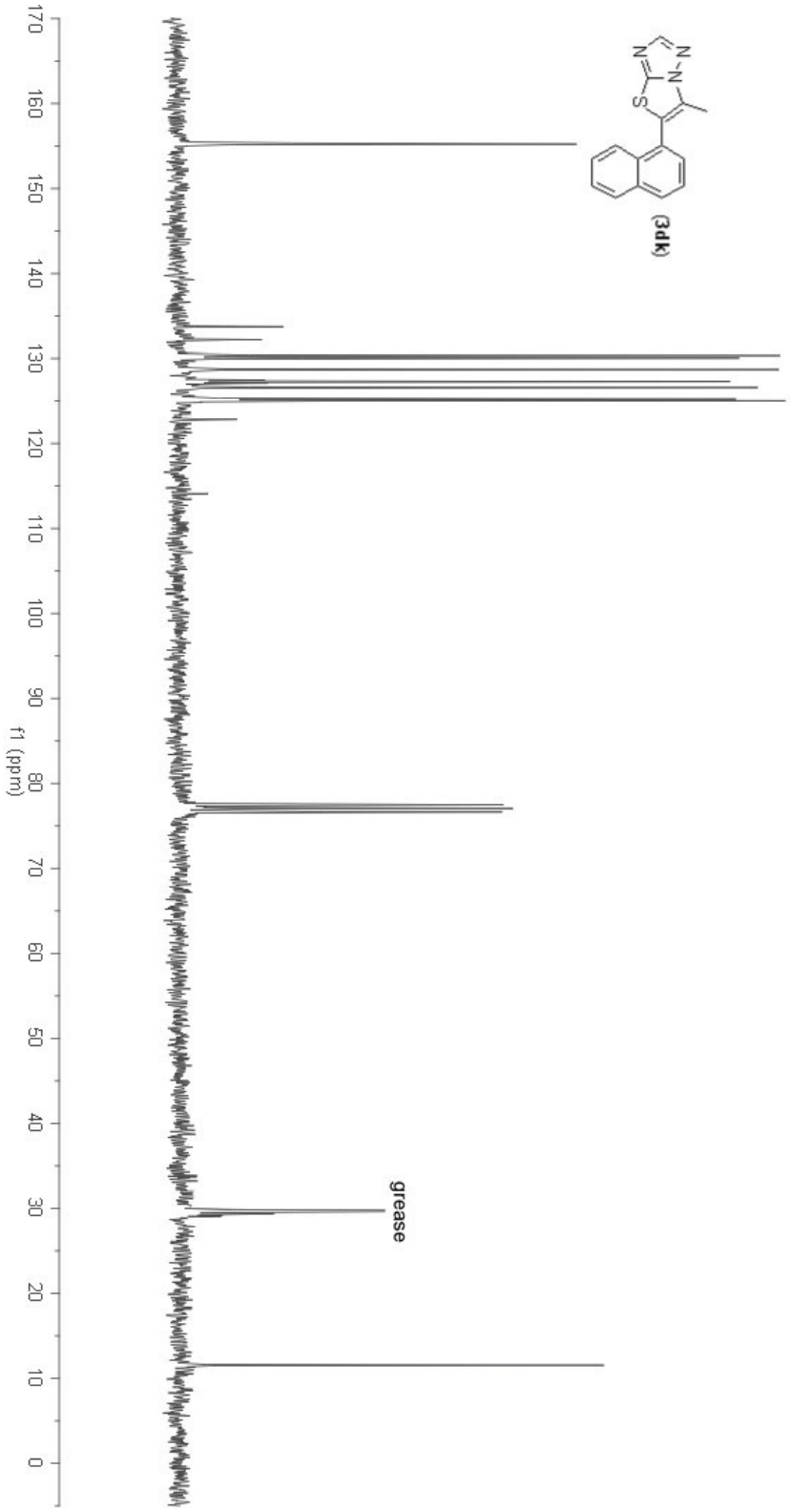
[^{13}C NMR Spectra of **3dk**]



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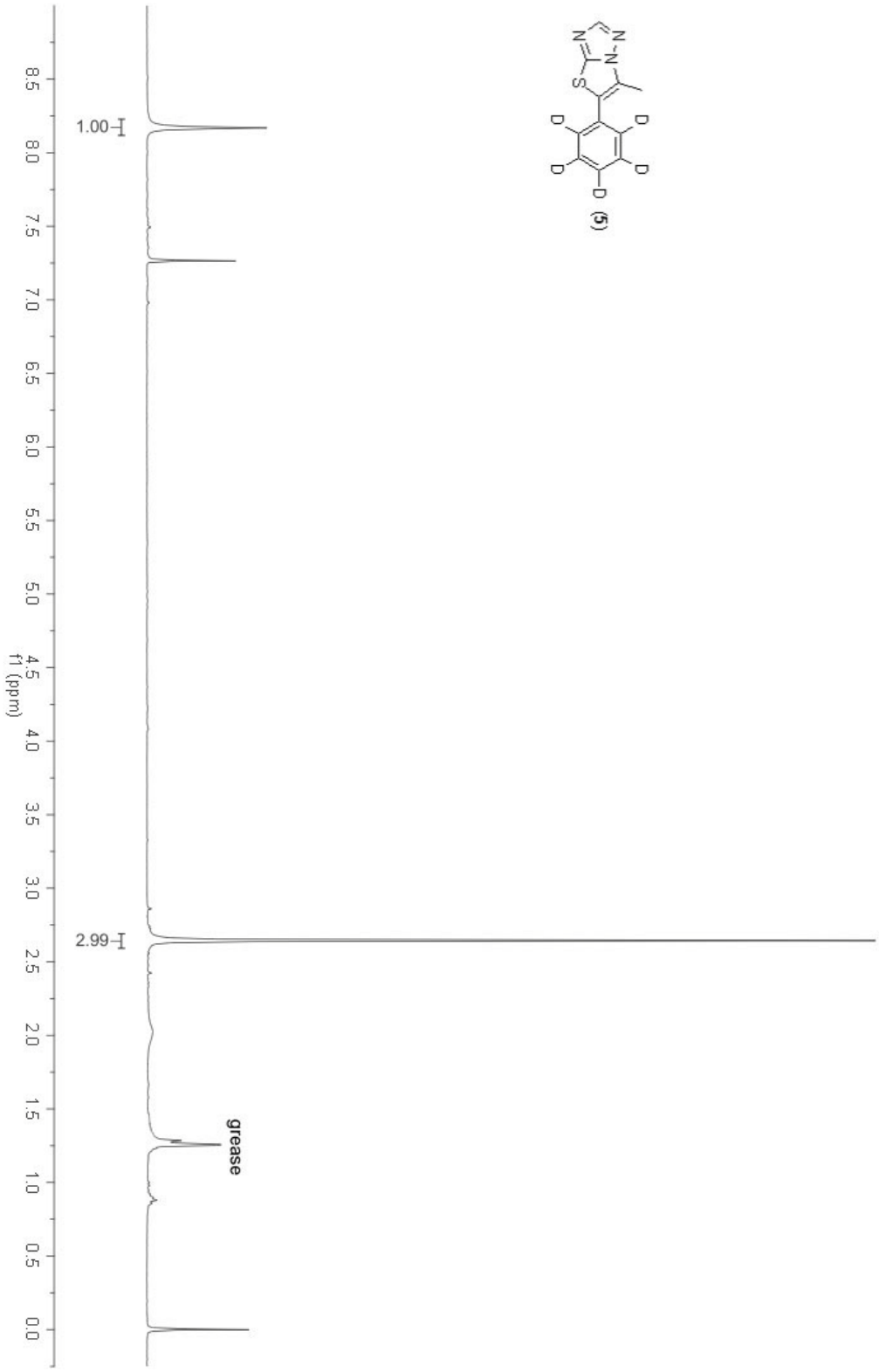
[^{1}H NMR Spectra of **5**]



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[^{13}C NMR Spectra of **5**]