Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

Redox activated amines in organophotoinduced alkylation of coumarins

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Experimental section

1. General Information. Nuclear magnetic resonance (NMR) spectra were recorded in deuterated solvents with residual protonated solvent signal as internal reference on a BrukerAva-300, BrukerAva-400 and BrukerAva-500. Chemical shifts are reported in parts per million using the solvent resonance internal standard (chloroform, 7.26 and 77.0 ppm). Data is reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, bs = broad singlet), coupling constant, and integration. Electrospray and electron impact high resolution mass spectrometry was performed by Bruker mass spectrometer. The data is recorded as the ionization method followed by the calculated and measured masses. Solvents for starting material preparation and coupling reactions were dried before use. Green LEDs (2.50 W, λ = 530 nm) Rebel LED, mounted on a 25 mm cool base was purchased from commercial supplier Luxeon Star LEDs Quadica Developments Inc.10-3447 30 Ave N. Lethbridge, Alberta T1H 7B5 Canada.

2. Preparation of Starting Materials

2.1. Preparation of Coumarins. Preparation of 3-Cyanocoumarins (1a−1e)

3-Cyanocoumarins were synthesized using known literature procedure.[1] To a solution of salicylaldehyde (10.0 mmol) and malononitrile (660 mg, 10.0 mmol) in EtOH (10.0 mL) was added NH_4OAc (462 mg, 6.0 mmol) slowly. The reaction mixture was stirred at room temperature for 4h to form the precipitations. Then the precipitate was filtered and washed with EtOH and dried in vacuum. Next, the products were dissolved in EtOH by gentle heating at 75 ˚C and then 1 mL HCl was added in reaction mixture. Whole solution was vigorously stirred at 75 °C for 30 min. After that the material was poured in ice water. The resulting solid was filtered and washed with cold water, subsequently dried under vacuum. The crude product was purified by column chromatography (ethyl acetate/Hexane =3:7-4:6).

2.1.1 Synthesis of coumarin-3-carboxylate (1f-1l)

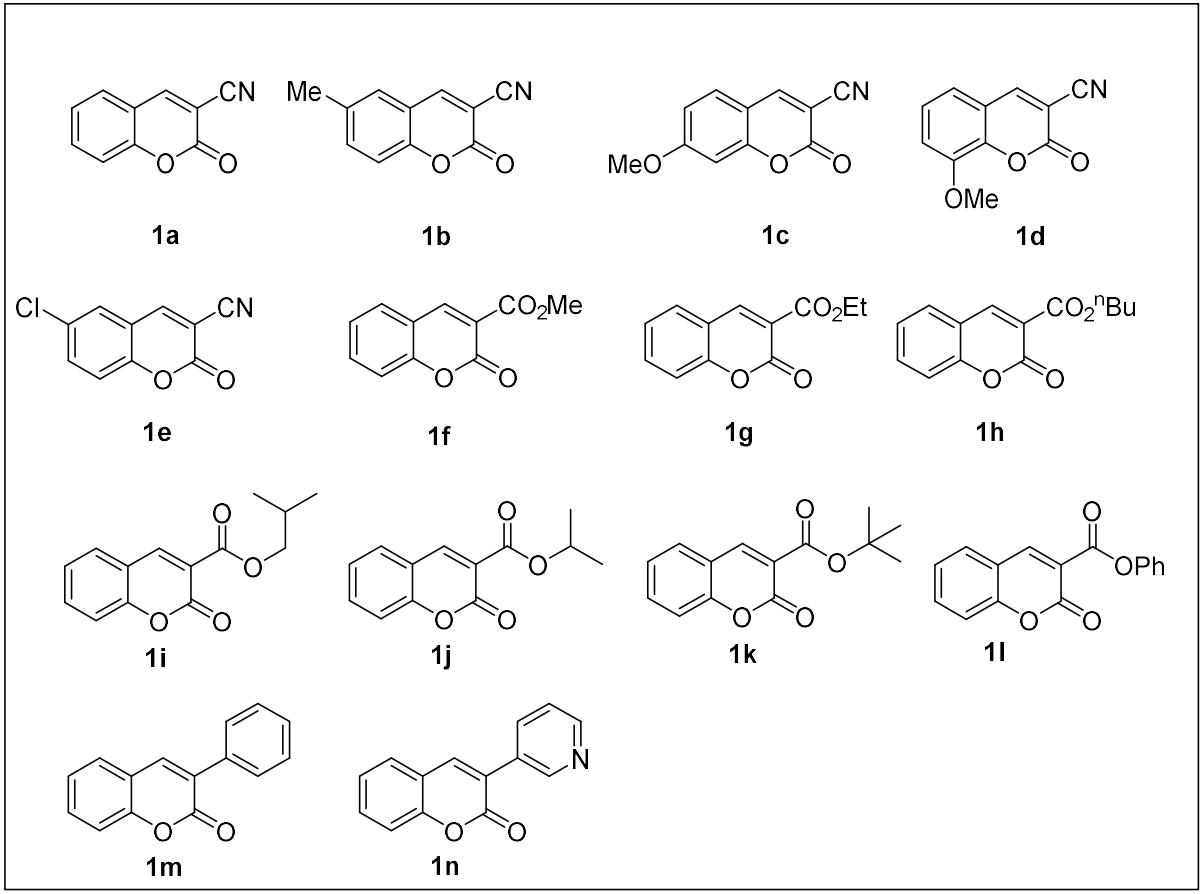
Ethyl coumarin-3-carboxylate **1g** was synthesized following known literature procedure.[2] To a solution of salicylaldehyde (1.83 g, 15 mmol) in 30 mL of ethanol was added diethyl malonate (2.88 g, 18 mmol), 2 drops of acetic acid and piperidine (0.15 mL). The reaction mixture was stirred under reflux for 8 h, After completion of the reaction, dilution was done with ice-cold water (50 mL)., the cake was filtered and washed with cold water. The product was dried under vacuum to give a white solid (3.07 g, 94% yield).

Coumarin-3-carboxylate **1f**,**1h-1l** were synthesized from known literature in three steps.[3]

2.1.2 Synthesis of 2H-Chromenones (1m-1n)

3-Phenyl-2H-chromen-2-one (**1m**) and 3-(Pyridin-3-yl)-2H-chromen-2-one (**1n**) was synthesized following known literature procedure.[4] Salicylaldehyde (1 mmol) and two equivalents of ^{t}BuOK were added in a 25 mL tube equipped with a stirring bar. Then, 1 mL of DMF and 2-phenylacetonitrile and 3-pyridineacetonitrile (1.5 mmol) were injected by syringe. After that, the tube was closed and heated up to 110 °C for 16 h. When the reaction was completed, the reaction mixture was cooled to room temperature and quenched with distilled water and the resulted solution was extracted with ethyl acetate and dried over $MgSO_4$. The crude product was purified by column chromatography (ethyl acetate/Hexane = 1:25–1:8).

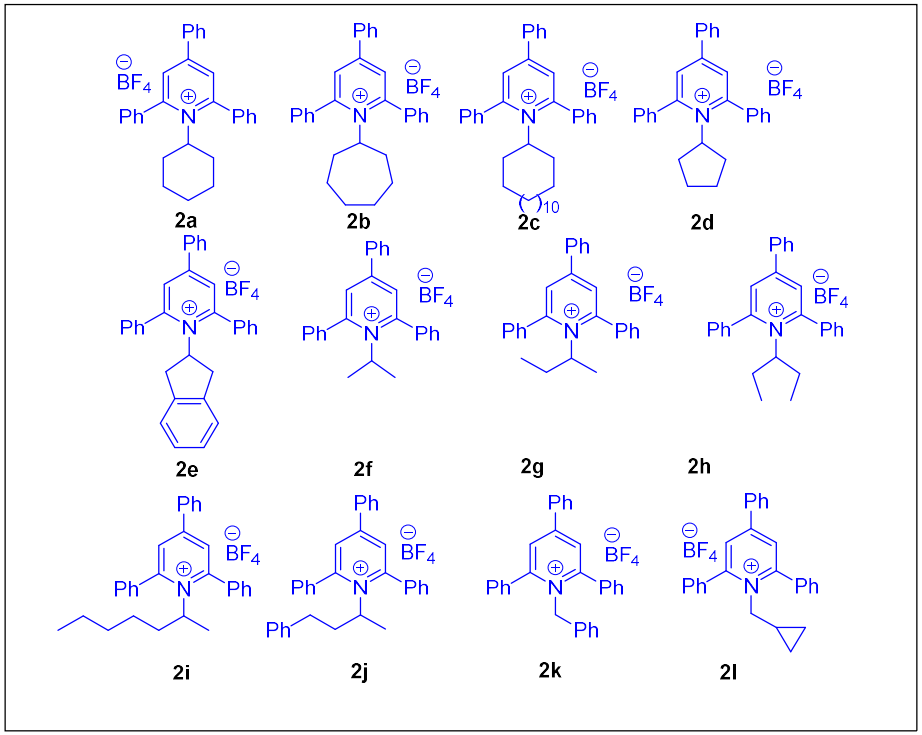
S1: Coumarin Substrate Scope (1a-1n):



2.2 Preparation of Pyridinium Salts

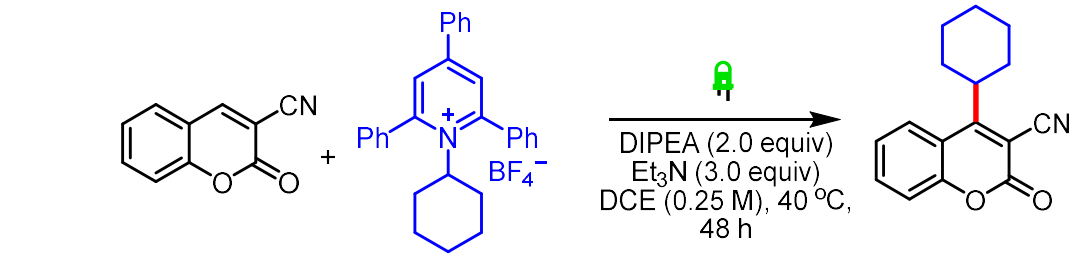
All Pyridinium Salts (**2**) were synthesized by following known literature procedure.[5] The respective primary amine (1.2 equiv.), 2,4,6-triphenylpyrylium tetrafluoroborate (1.0 equiv.) and EtOH were mixed in a flask with a magnetic stirring bar. The reaction mixture was refluxed in oil bath at 80 ˚C for 4 h. After completion of reaction the mixture was then allowed to cool at room. After that solution is diluted with Et_2O (2-3x volume of EtOH used) and vigorously stirred for 2 h. The white resulting solid was filtered and washed with Et_2O (3x 25 mL).

S2: Katritzky pyridinium salt Substrate Scope (2a-2l)


2a
2b
2c
2d
2e
2f
2g
2h
2i
2j
2k
2l

3: Optimization

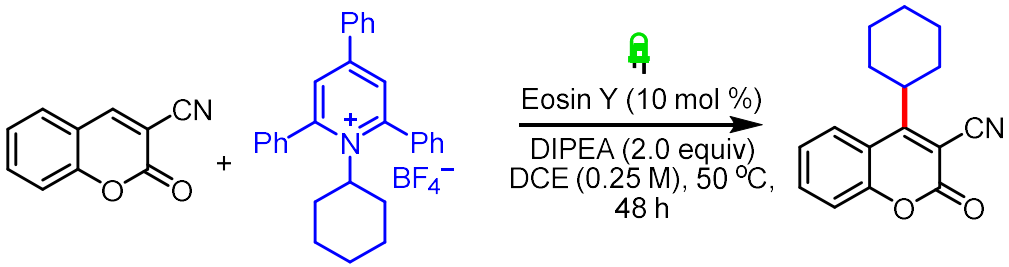
S3.1: Optimization of Catalyst loading



EOSIN Y **1a** **2a** **3a**

mol%	Yield (%)
2.5	42
5	54
10	65

S3.2: Optimization of Et_3N

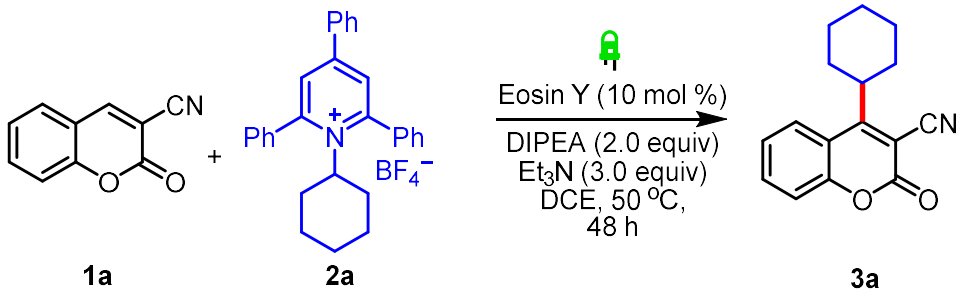


1a **2a** **3a**

Et_3N

Equiv	Yield (%)
2	48
3	65
4	60

S3.3: Optimization for concentration of reaction

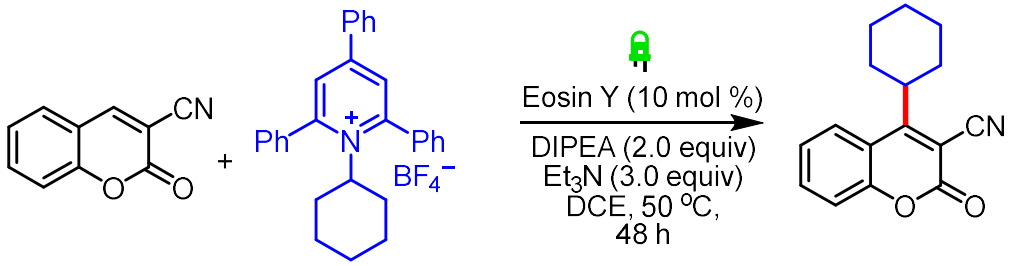


1a **2a** **3a**

Concentration

Entry	Concentration (M)	Yield (%)
1	0.4	56
2	0.13	55
3	0.1	65
4	0.05	32

S3.4: Optimization of substrate loading

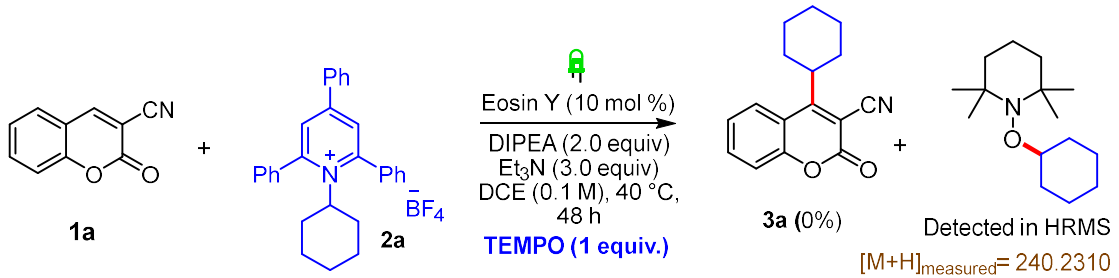


1a **2a** **3a**

Equiv. of **2a**

Equiv	Yield (%)
1	32
1.2	38
1.5	52
2	65
3	63

4. Control Experiment



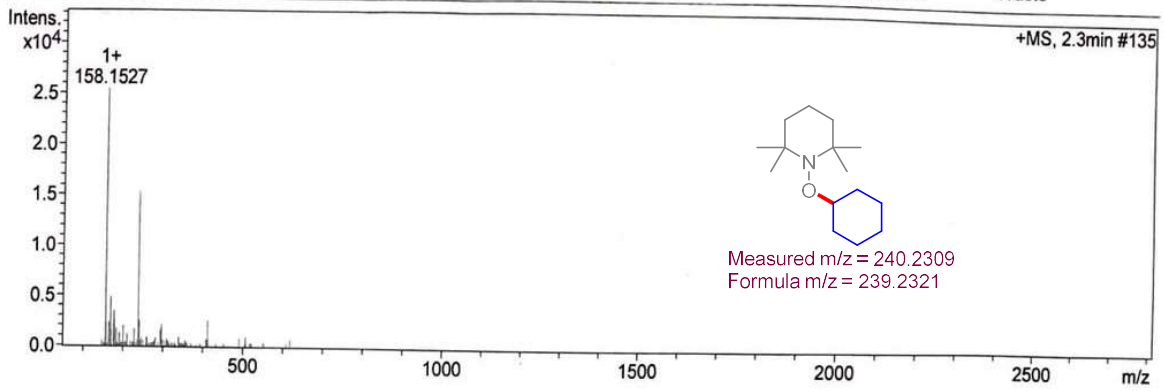
Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	Y:\Data\JUNE2022\RPS CYCLOHEX000001.d	Acquisition Date	06/16/22 2:55:09 PM
Method	tune_low.m		
Sample Name	tm 1 100	Operator	BDAL@DE
Comment		Instrument	micrOTOF-Q 228888.10262

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	2800 m/z	Set Collision Cell RF	250.0 Vpp	Set Divert Valve	Waste



Meas. m/z	#	Ion Formula	m/z	err [ppm]	Mean err [ppm]	rdb	N-Rule	e⁻ Conf	mSigma	Std I	Std Mean m/z	Std I VarNorm	Std m/z Diff	Std Comb Dev
240.230953	1	C15H30NO 240.232191		5.2	10.0	1.5	ok	even	2.4	4.9	n.a.	n.a.	n.a.	n.a.

5. General methods of deaminative alkylation reaction

Coumarin (0.4 mmol, 2.0 equiv.), Pyridinium Salts (0.2 mmol, 1 equiv.) were taken in a long neck round bottom flask and 10 mol % of Eosin Y was added into it, the RB was capped with septum. After that, 2.0 equiv. of DIPEA and 3.0 equiv. of Et_3N followed by 2 mL of dry DCE were added into the reaction mixture via a syringe. The mixture was degassed and filled with N_2 (three times). The reaction mixture was irradiated with green LED for 48 h. The light system was covered with aluminium foil so that heat should maintain during reaction period. After completion (monitored through TLC), reaction was quenched with water and extracted with DCM (3 x 10 mL), washed with brine solution. After removal of solvent in vacuo, the product was purified by silica gel chromatography using EtOAc-hexane (1:9 to 4:6) as eluent to provide the desired product **3**.

4-cyclohexyl-2-oxo-2*H*-chromene-3-carbonitrile (3a): Physical state: white solid; **Yield**: 33 mg (65 %). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 (s, 1H), 7.67 (t, *J* = 7.8 Hz, 1H), 7.38 (t, *J* = 7.5 Hz, 2H), 3.33 (s, 1H), 2.23-2.17 (m, 2H), 1.97 (d, *J* = 7.1 Hz, 2H), 1.86 (d, *J* = 10.6 Hz, 3H), 1.45 (t, *J* = 8.9 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 169.9, 157.7, 153.7, 135.0, 125.3, 118.2, 117.4, 114.2, 100.8, 29.9, 26.5, 25.4. **HRMS (ESI/QTOF), m/z:** $[M+Na]^+$ Calcd. For $C_{16}H_{15}NO_2Na$, 276.0994; Found: 276.0991.

4-cycloheptyl-2-oxo-2H-chromene-3-carbonitrile (3b): Physical state: white solid: **Yield**: 27 mg (50 %). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.2 Hz, 1H), 7.67 (s, 1H), 7.40 (d, *J* = 8.3 Hz, 2H), 1.95 (s, 4H), 1.75-1.69 (m, 6H), 1.58 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 124.9, 118.4, 32.8, 29.9, 28.2. **HRMS (ESI/QTOF), m/z:** $[M+Na]^+$ Calcd. For $C_{17}H_{17}NO_2Na$ 290.1151; Found: 290.1157.

4-cyclopentadecyl-2-oxo-2*H*-chromene-3-carbonitrile (3c): Physical state: white solid; **Yield**: 54 mg (72 %). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.3 Hz, 1H), 7.73 – 7.60 (m, 1H), 7.49 – 7.30 (m, 2H), 3.40 (bs, 1H), 2.10 (dd, *J* = 18.5, 11.5 Hz, 2H), 1.88 (d, *J* = 5.9 Hz, 2H), 1.67-1.37 (m, 24H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 170.4, 153.9, 134.5, 127.8, 125.5, 124.7, 118.3, 116.6, 113.7, 102.2, 45.5, 34.4, 32.0, 27.4, 26.8, 26.6, 26.5, 26.4. **HRMS (ESI/QTOF), m/z:** $[M+Na]^+$ Calcd. For $C_{25}H_{33}NO_2Na$, 402.2403; Found: 402.2398.

4-cyclopentyl-2-oxo-2*H*-chromene-3-carbonitrile (3d): Physical state: brown solid **Yield**: 27 mg (58 %). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.1 Hz, 1H), 7.68 (t, *J* = 7.8 Hz, 1H), 7.39 (dd, *J* = 15.6, 7.9 Hz, 2H), 3.88 – 3.64 (m, 1H), 2.26 – 2.04 (m, 6H), 1.90 (s, 2H); **^{13}C NMR** (75MHz, $CDCl_3$) δ 170.5, 157.5, 153.8, 134.9, 126.1, 125.1, 118.5, 117.3, 113.9, 101.3, 43.1, 33.4, 27.7; **HRMS (ESI/QTOF), m/z:** $[M+Na]^+$ Calcd. For $C_{15}H_{13}NO_2Na$, 262.0838; Found: 262.0836.

4-(2,3-dihydro-1H-inden-2-yl)-2-oxo-2*H*-chromene-3-carbonitrile (3e): Physical state: brown solid; **Yield**: 35 mg (62 %). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.67 – 7.64 (m, 1H), 7.51 (d, *J* = 7.5 Hz, 1H), 7.43 (d, *J* = 8.3 Hz, 1H), 7.31 (s, 4H), 7.22 (t, *J* = 7.7 Hz, 1H), 4.58 – 4.41 (m, 1H), 3.64-3.51 (m, 4H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.9, 156.9, 153.9, 140.7, 134.9, 127.7, 126.3, 125.3, 118.6, 116.4, 113.6, 102.3, 41.9, 39.9; **HRMS (ESI/QTOF), m/z:** $[M+Na]^+$ Calcd. For $C_{19}H_{13}NO_2Na$, 310.0838; Found: 310.0849.

4-isopropyl-2-oxo-2*H*-chromene-3-carbonitrile (3f): Physical state: brown solid **Yield**: 23 mg (60 %). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.1 Hz, 1H), 7.69 (t, *J* = 7.8 Hz, 1H), 7.40 (t, *J* = 8.6 Hz, 2H), 3.75 (dt, *J* = 14.3, 7.1 Hz, 1H), 1.61 (d, *J* = 7.2 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.4, 157.6, 153.8, 135.0, 126.1, 125.3, 118.4, 117.1, 113.9, 100.8, 29.8, 20.8; **HRMS (ESI/QTOF), m/z:** $[M+Na]^+$ Calcd. For $C_{13}H_{12}NO_2Na$, 214.0862; Found: 214.0874.

4-(sec-butyl)-2-oxo-2*H*-chromene-3-carbonitrile (3g): Physical state: white solid; **Yield**: 26 mg (58 %). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 6.7 Hz, 1H), 7.69 (t, *J* = 7.7 Hz, 1H), 7.40 (dd, *J* = 15.4, 7.9 Hz, 2H), 3.50 (s, 1H), 2.08 – 1.97 (m, 2H), 1.58 (d, *J* = 7.1 Hz, 3H), 0.97 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.8, 157.4, 153.8, 134.9, 125.2, 118.4, 113.9, 21.6, 14.0; **HRMS (ESI/QTOF), m/z:** $[M+Na]^+$ Calcd. For $C_{14}H_{13}NO_2Na$, 250.0838; Found: 250.0846.

2-oxo-4-(pentan-3-yl)-2H-chromene-3-carbonitrile (3h): Physical state: light yellow solid; **Yield**: 35 mg (73 %). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.97 (dd, *J* = 24.6, 8.3 Hz, 1H), 7.69 (dt, *J* = 22.1, 7.8 Hz, 1H), 7.39 (dd, *J* = 31.1, 8.1 Hz, 2H), 3.32 (dt, *J* = 35.9, 7.2 Hz, 1H), 2.22 – 1.97 (m, 4H), 0.93 (dt, *J* = 22.4, 7.4 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 170.9, 168.9, 156.9, 153.7, 135.3, 134.8, 126.9, 125.5, 124.9, 119.4, 118.5, 118.2, 116.7, 113.9, 104.1, 51.4, 43.4, 28.2, 26.4, 12.9**. HRMS (ESI/QTOF), m/z:** $[M+Na]^+$ Calcd. For $C_{15}H_{15}NO_2Na$ 264.0095; Found: 264.0094.

4-(heptan-2-yl)-2-oxo-2*H*-chromene-3-carbonitrile (3i): Physical state: orange sticky solid; **Yield**: 33 mg (61 %). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.69 (t, *J* = 7.1 Hz, 1H), 7.41 (t, *J* = 8.4 Hz, 2H), 3.57 (s, 1H), 2.08 – 1.90 (m, 2H), 1.57 (d, *J* = 7.1 Hz, 3H), 1.28-1.25 (m, 6H), 0.85 (t, *J* = 6.6 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 171.2, 157.8, 153.7, 134.9, 127.2, 125.3, 118.41, 113.9, 31.7, 29.8, 28.0, 22.5, 14.1; **HRMS (ESI/QTOF), m/z:** $[M+Na]^+$ Calcd. For $C_{17}H_{19}NO_2Na$, 292.1308; Found: 292.1328.

2-oxo-4-(4-phenylbutan-2-yl)-2H-chromene-3-carbonitrile (3j) Physical state: yellow oil**; Yield**: 27 mg (45 %). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 (ddd, *J* = 8.6, 7.2, 1.5 Hz, 1H), 7.39 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.33 (d, *J* = 7.9 Hz, 1H), 7.28 – 7.14 (m, 4H), 7.10 (dd, *J* = 6.8, 1.9 Hz, 2H), 3.72-3.56 (m, 1H), 2.76 (s, 1H), 2.61 (s, 1H), 2.44 (s, 1H), 2.30 (dt, *J* = 14.9, 7.3 Hz, 1H), 1.60 (d, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 153.8, 140.4, 135.0, 128.7, 128.5, 126.6, 125.2, 118.4, 29.8. **HRMS (ESI/QTOF), m/z:** $[M+Na]^+$ Calcd. For $C_{20}H_{17}NO_2Na$ 326.1151; Found 326.1152.

4-benzyl-2-oxo-2*H*-chromene-3-carbonitrile (3k): Physical state: white solid **Yield**: 18 mg (34 %).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.0 Hz, 1H), 7.68 (t, *J* = 7.8 Hz, 1H), 7.42 (d, *J* = 8.2 Hz, 1H), 7.38 – 7.28 (m, 6H), 4.51 (s, 2H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.6, 156.9, 154.1, 135.2, 135.1, 129.5, 128.4, 127.9, 127.0, 125.6, 118.0, 117.7 113.8, 103.4, 37.7; **HRMS (ESI/QTOF), m/z:** $[M+H]^+$ Calcd. For For $C_{17}H_{12}NO_2$, 262.0863; Found: 262.0880

4-cyclohexyl-6-methyl-2-oxo-2*H*-chromene-3-carbonitrile (3l): Physical state: white solid; **Yield**: 33 mg (62 %). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71 (s, 1H), 7.50 (d, *J* = 8.2 Hz, 1H), 7.38 – 7.20 (m, 1H), 3.31 (s, 1H), 2.49 (s, 3H), 2.25-2.18 (m, 2H), 2.05 – 1.95 (m, 2H), 1.86 (s, 3H), 1.57 – 1.41 (m, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 169.9, 158.0, 151.9, 136.2, 135.1, 124.8, 118.0, 117.1, 114.5, 100.4, 29.8, 26.6, 25.4, 21.3; **HRMS (ESI/QTOF), m/z: HRMS (ESI/QTOF), m/z:** $[M+Na]^+$ Calcd. For $C_{17}H_{17}NO_2Na$, 290.1151; Found: 290.1168

4-cyclohexyl-7-methoxy-2-oxo-2*H*-chromene-3-carbonitrile (3m): Physical state: white solid; **Yield**: 40 mg (72 %). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85 (s, 1H), 6.93 (dd, *J* = 9.1, 2.2 Hz, 1H), 6.82 (d, *J* = 2.5 Hz, 1H), 3.91 (s, 3H), 3.24 (bs, 1H), 2.21-2.16 (m, 2H), 1.95 (d, *J* = 7.4 Hz,

2H), 1.82 (s, 3H), 1.42 (d, *J* = 7.2 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.3, 157.4, 148.2, 143.6, 124.9, 118.1, 116.4, 114.4, 100.9, 56.6, 29.8, 26.6, 25.4; **HRMS (ESI/QTOF), m/z:** $[M+H]^+$ Calcd. For For $C_{17}H_{18}NO_3$, 284.1281; Found: 284.1275

4-cyclohexyl-8-methoxy-2-oxo-2*H*-chromene-3-carbonitrile (3n): Physical state: white solid; **Yield**: 37 mg (65 %). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54 (s, 1H), 7.33 (t, *J* = 8.2 Hz, 1H), 7.25 (t, *J* = 10.1 Hz, 1H), 3.98 (s, 3H), 3.30 (s, 1H), 2.23-2.18 (m, 2H), 1.98 (d, *J* = 7.3 Hz, 2H), 1.85 (s, 3H), 1.44 (d, *J* = 8.2 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.3, 157.4, 148.2, 143.6, 124.9, 118.1, 116.4, 114.4, 100.8, 56.6, 29.8, 26.6, 25.4; **HRMS (ESI/QTOF), m/z:** $[M+Na]^+$ Calcd. For $C_{17}H_{17}NO_3Na$, 306.1100; Found: 306.1095.

6-chloro-4-cyclohexyl-2-oxo-2*H*-chromene-3-carbonitrile (3o): Physical state: white solid **Yield**: 20 mg (35 %). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.63 (dd, *J* = 8.8, 2.1 Hz, 1H), 7.36 (d, *J* = 8.8 Hz, 1H), 3.19 (s, 1H), 2.22 (s, 2H), 2.03 – 1.97 (m, 2H), 1.87 (s, 3H), 1.44 (dd, *J* = 17.8, 6.2 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 168.7, 157.1, 152.1, 134.8, 131.0, 124.9, 119.7, 118.6, 113.9, 102.3, 29.8, 26.5, 25.4; **HRMS (ESI/QTOF), m/z:** $[M+Na]^+$ Calcd. For $C_{16}H_{14}ClNO_2Na$, 310.0605; Found: 310.0615

Methyl 4-cyclohexyl-2-oxochromane-3-carboxylate (3p): Physical state: sticky solid**; Yield**: 43 mg (75 %). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.31 – 7.26 (m, 1H), 7.16 – 7.06 (m, 3H), 3.97 (d, *J* = 1.3 Hz, 1H), 3.59 (s, 3H), 3.16 (d, *J* = 7.8 Hz, 1H), 1.84 (d, *J* = 12.5 Hz, 1H), 1.80 – 1.75 (m, 1H), 1.74 – 1.68 (m, 1H), 1.62 (dd, *J* = 23.1, 10.9 Hz, 2H), 1.48 – 1.39 (m, 1H), 1.23 – 0.98 (m, 5H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.0, 164.8, 150.8, 129.8, 128.6, 124.3, 122.9, 116.9, 52.9, 49.5, 45.7, 41.3, 30.4, 29.8, 25.9, 25.8. **HRMS (ESI/QTOF), m/z:** $[M+Na]^+$ Calcd. $C_{17}H_{20}NaO_4$ 311.1254: Found 311.1251.

Ethyl 4-cyclohexyl-2-oxochromane-3-carboxylate (3q): Physical state: liquid**; Yield**: 54 mg (90 %). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.31 – 7.26 (m, 1H), 7.17 – 7.07 (m, 3H), 4.08 (dq, *J* = 10.8, 7.1 Hz, 1H), 4.02 – 3.97 (m, 1H), 3.95 (d, *J* = 1.6 Hz, 1H), 3.13 (dd, *J* = 8.1, 1.3 Hz, 1H), 1.87 (d, *J* = 12.5 Hz, 1H), 1.78 (dd, *J* = 9.6, 6.4 Hz, 1H), 1.75 – 1.69 (m, 1H), 1.67 – 1.58 (m, 2H), 1.47 – 1.39 (m, 1H), 1.26 – 1.03 (m, 5H), 1.00 (t, *J* = 7.1 Hz, 3H).; **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.8, 165.3, 151.2, 129.9, 128.8, 124.4, 123.3, 117.1, 62.2, 49.9, 46.2, 41.3, 30.7, 30.1, 26.1, 13.9. **HRMS (ESI/QTOF), m/z:** $[M+Na]^+$ Calcd. For $C_{18}H_{22}NO_4Na$, 325.1410; Found: 325.1415.

Butyl 4-cyclohexyl-2-oxochromane-3-carboxylate (3r): Physical state: white solid**; Yield**: 55 mg (83 %). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.28 – 7.24 (m, 1H), 7.14 – 7.04 (m, 3H), 4.02 (dt, *J* = 10.7, 6.5 Hz, 1H), 3.95 – 3.87 (m, 2H), 3.11 (dd, *J* = 8.1, 1.7 Hz, 1H), 1.84 (dd, *J* = 12.6, 3.3 Hz, 1H), 1.76 (dd, *J* = 13.7, 2.9 Hz, 1H), 1.73 – 1.67 (m, 1H), 1.65 – 1.55 (m, 2H), 1.45 – 1.37 (m, 1H), 1.37 – 1.27 (m, 2H), 1.20 – 0.97 (m, 7H), 0.76 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.6, 164.9, 150.9, 129.7, 128.5, 124.1, 122.9, 116.8, 65.7, 49.7, 45.9, 41.1, 30.4, 30.1, 29.8, 25.9, 25.8, 18.5, 13.3. **HRMS (ESI/QTOF), m/z:** $[M+Na]^+$ Calcd. $C_{20}H_{26}O_4Na$ 353.1723; Found 353.1727.

Isobutyl 4-cyclohexyl-2-oxochromane-3-carboxylate (3s): Physical state: white solid**; Yield**: 52 mg (79 %). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29 – 7.23 (m, 1H), 7.15 – 7.04 (m, 3H), 3.95 (d, *J* = 1.7 Hz, 1H), 3.80 (dd, *J* = 10.6, 6.6 Hz, 1H), 3.70 (dd, *J* = 10.6, 6.3 Hz, 1H), 3.12 (dd, *J* = 8.0, 1.7 Hz, 1H), 1.88 – 1.81 (m, 1H), 1.77 – 1.56 (m, 5H), 1.48 – 1.38 (m, 1H), 1.21 – 0.96 (m, 5H), 0.71 (d, *J* = 6.8 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.9, 165.2, 151.1, 130.0, 128.8, 124.4, 123.2, 117.1, 72.1, 49.9, 46.2, 41.4, 30.6, 30.1, 27.6, 26.1, 18.7. **HRMS (ESI/QTOF), m/z:** $[M+Na]^+$ Calcd. $C_{20}H_{26}O_4Na$ 353.1723: Found 353.1722.

Isopropyl 4-cyclohexyl-2-oxochromane-3-carboxylate (3t): **Physical state**: white solid**; Yield**: 49 mg (78 %). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.27 (ddd, *J* = 9.9, 6.9, 1.9 Hz, 1H), 7.17 – 6.99 (m, 3H), 4.83 (hept, *J* = 6.3 Hz, 1H), 3.91 (d, *J* = 1.7 Hz, 1H), 3.07 (dd, *J* = 8.4, 1.6 Hz, 1H), 1.87 (d, *J* = 12.5 Hz, 1H), 1.80 – 1.73 (m, 1H), 1.70 (dd, *J* = 6.9, 2.6 Hz, 1H), 1.66 – 1.54 (m, 2H), 1.45 – 1.36 (m, 1H), 1.24 – 1.10 (m, 3H), 1.09 (d, *J* = 6.3 Hz, 3H), 1.02 (ddd, *J* = 23.2, 11.7, 3.4 Hz, 2H), 0.84 (d, *J* = 6.2 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.1, 165.2, 151.1. 129.7, 128.5, 124.1, 123.2, 116.7, 69.8, 49.9, 46.2, 40.9, 30.5, 29.9, 25.9, 21.2, 20.9. **HRMS (ESI/QTOF), m/z:** $[M+Na]^+$ Calcd. $C_{19}H_{24}O_4Na$ 339.1567; Found 339.1566.

***tert*-butyl 4-cyclohexyl-2-oxochromane-3-carboxylate (3u): Physical state**: white stick solid**; Yield**: 52 mg (79 %). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.29 – 7.25 (m, 1H), 7.13 – 7.05 (m, 3H), 3.85 (d, *J* = 1.8 Hz, 1H), 3.02 (dd, *J* = 8.6, 1.9 Hz, 1H), 1.86 (ddd, *J* = 12.4, 4.6, 2.3 Hz, 1H), 1.78 – 1.73 (m, 1H), 1.71 – 1.65 (m, 1H), 1.65 – 1.60 (m, 1H), 1.58 (ddd, *J* = 10.7, 5.3, 2.2 Hz, 1H), 1.42 – 1.34 (m, 1H), 1.19 (dd, *J* = 12.8, 3.3 Hz, 1H),

1.14 (s, 9H), 1.12 – 1.05 (m, 2H), 1.00 (ddd, *J* = 19.4, 11.7, 3.5 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.9, 165.7, 151.5, 130.1, 128.7, 124.2 123.8, 116.9, 83.5, 50.9, 46.8, 40.9, 30.8, 30.2, 27.5, 26.1. **HRMS (ESI/QTOF), m/z:** $[M+Na]^+$ Calcd.$C_{20}H_{26}O_4Na$ 353.1723; Found 353.1725.

4-cyclohexyl-3-phenylchroman-2-one (3v): Physical state: white liquid**; Yield**: 25 mg (41 %). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.45 – 7.40 (m, 3H), 7.39 – 7.28 (m, 2H), 7.20 – 7.11 (m, 3H), 7.07 (t, *J* = 6.3 Hz, 1H), 4.13 (d, *J* = 6.5 Hz, 1H), 2.97 (dd, *J* = 6.4, 3.0 Hz, 1H), 1.89 (d, *J* = 12.7 Hz, 1H), 1.63 (m, 3H), 1.54 (d, *J* = 13.1 Hz, 1H), 1.37 (t, *J* = 12.8 Hz, 1H), 1.20 – 1.07 (m, 3H), 0.95 – 0.85 (m, 1H), 0.70 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 169.9, 151.9, 134.8, 130.1, 129.7, 128.6, 127.7, 127.2, 125.2, 123.8, 116.9, 49.1, 37.7, 32.2, 26.9, 26.5, 25.9. **HRMS (ESI/QTOF), m/z:** $[M+K]^+$ Calcd. $C_{21}H_{22}O_2K$, 345.1251; Found: 345.1242.

4-cyclohexyl-3-(pyridin-3-yl) chroman-2-one (3w): Physical state: white liquid**; Yield**: 16 mg (26 %). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.42 (dd, *J* = 13.0, 3.7 Hz, 2H), 7.34 (dt, *J* = 8.2, 2.0 Hz, 1H), 7.29 – 7.26 (m, 1H), 7.14 – 7.06 (m, 4H), 4.31 (s, 1H), 2.92 (d, *J* = 6.4 Hz, 1H), 1.91 (dt, *J* = 12.5, 3.3 Hz, 1H), 1.82 – 1.72 (m, 2H), 1.63 (ddt, *J* = 14.4, 10.9, 3.7 Hz, 3H), 1.24 – 1.07 (m, 5H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 168.6, 151.3, 149.1, 148.9, 134.9, 133.2, 130.6, 129.2, 125.1, 123.9, 122.9, 117.2, 49.6, 46.5, 43.5, 30.7, 30.4, 26.6, 26.5, 26.4; **HRMS (ESI/QTOF), m/z:** $[M+H]^+$ Calcd. $C_{20}H_{22}NO_2$, 308.1645; Found: 308.1639.

4-cyclohexyl-*N*, *N*-diethyl-2-oxochromane-3-carboxamide (3x): Physical state: white solid**; Yield**: 45 mg (68 %). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.26 (dt, *J* = 6.1, 2.8 Hz, 1H), 7.07 (dt, *J* = 7.1, 6.3 Hz, 3H), 4.14 (s, 1H), 3.96 (dt, *J* = 13.2, 6.6 Hz, 1H), 3.30 (dt, *J* = 13.4, 6.7 Hz, 1H), 2.77 (d, *J* = 6.9 Hz, 1H), 1.85 (d, *J* = 12.4 Hz, 1H), 1.79 – 1.42 (m, 6H), 1.32 – 1.25 (m, 9H), 1.22 – 1.07 (m, 3H), 1.03 (t, *J* = 6.0 Hz, 3H), 0.99 (dt, *J* = 12.5, 4.0 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.6, 166.2, 151.7, 129.2, 128.7, 124.1, 122.7, 116.9, 49.6, 46.5, 42.9, 30.7, 30.1, 26.3, 21.2, 20.9, 20.5, 20.0. **HRMS (ESI/QTOF), m/z:** $[M+Na]^+$ Calcd. $C_{20}H_{31}NO_3Na$ 380.2202; Found 380.2254.

4-(but-3-en-1-yl)-2-oxo-2*H*-chromene-3-carbonitrile (3y): Physical state: white solid; **Yield**: 26 mg (58 %). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.78 – 7.68 (m, 2H), 7.46 – 7.38 (m, 2H), 5.90 (ddt, *J* = 17.1, 10.5, 6.8 Hz, 1H), 5.16 – 5.00 (m, 2H), 3.29 – 3.13 (m, 2H), 2.52 (dt, *J* = 14.4, 7.1 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.7, 156.9, 153.9, 135.3, 135.1 125.9, 125.6, 118.2, 117.6, 117.4, 113.5, 102.3, 33.6, 31.4; **HRMS (ESI/QTOF), m/z:** $[M+Na]^+$ Calcd. For $C_{14}H_{11}NO_2Na$, 248.0681; Found: 248.0687.

6. Crystallographic data

Sample preparation: Single crystal of compound **3d** suitable for the X-ray diffraction studies were grown from its EtOH/Heptane solution at room temperature.

Molecular structure determination of compounds **3d**: Single crystal X-ray diffraction data for compound **3c** was collected using a Bruker SMART APEX diffractometer equipped with a 3-axis goniometer. The crystals were covered with Paratone–*N* and mounted a glass capillary. The data were collected at room temperature using Mo Kα radiation (λ = 0.71073). Integration of data was performed using SAINT. Empirical absorption correction was applied using SADABS. Structure solutions were accomplished by directs methods and refine by full matrix least-square on F2 using OLEX2. All non-hydrogen atoms were refined anisotropically. The position of hydrogen atoms was fixed according to a riding model and were refined isotropically.

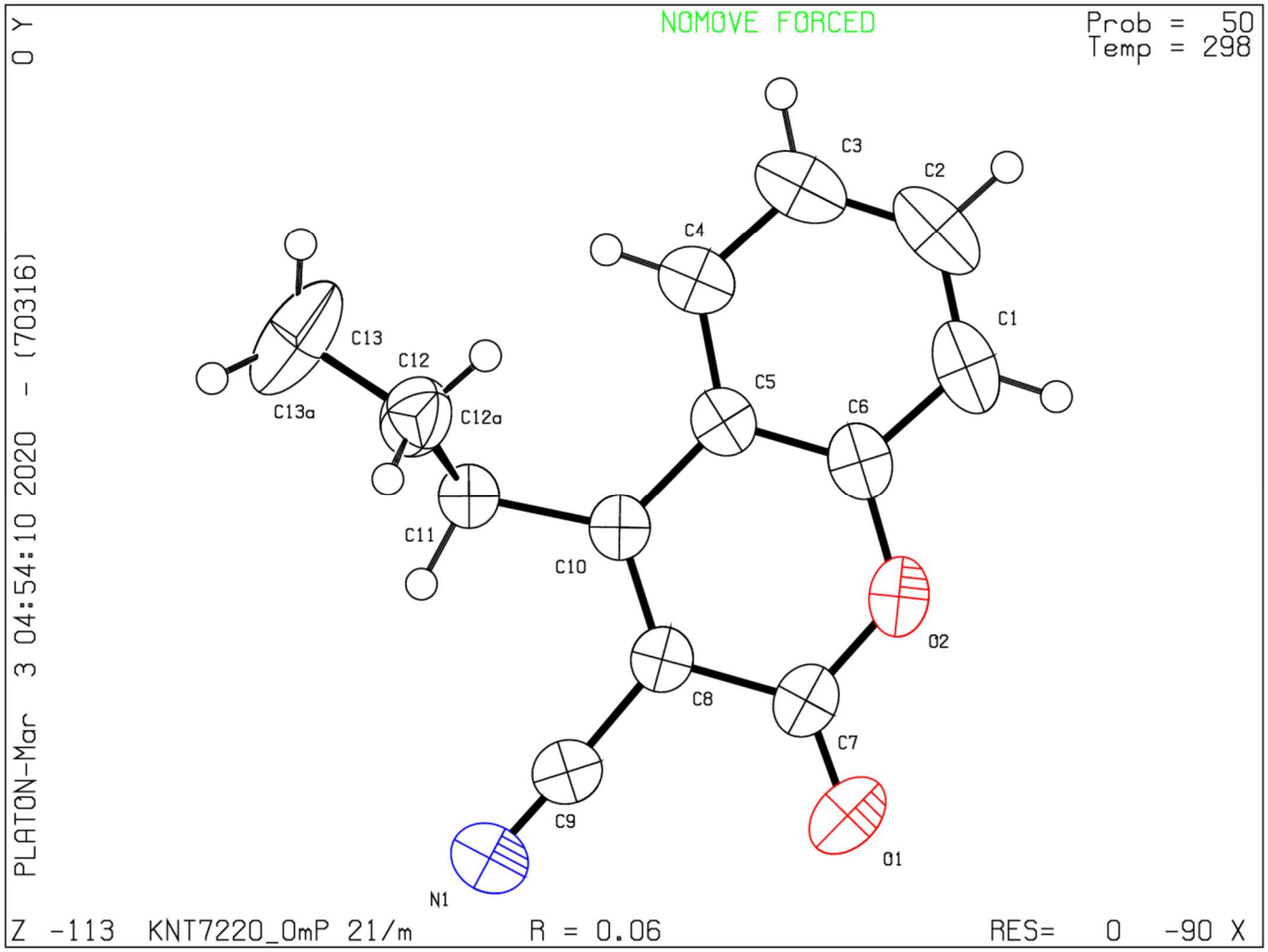


Fig. 1 Single Crystal X-ray Structure of Compound **3d**.

Table S1. Crystal data and structure refinement for 3d

Bond precision:	C-C = 0.0039 A		Wavelength=0.71073
Cell:	a=8.805(3)	b=6.864(2)	c=10.545(4)
	alpha=90	beta=110.673(10)	gamma=90
Temperature:	298 K		

	Calculated	Reported
Volume	596.3(4)	596.3(4)
Space group	P 21/m	P 21/m
Hall group	-P 2yb	-P 2yb
Moiety formula	C_{15} H_{13} N O_2	C_{15} H_{13} N O_2
Sum formula	C_{15} H_{13} N O_2	C_{15} H_{13} N O_2
Mr	239.26	239.26
Dx,g cm-3	1.333	1.333
Z	2	2
Mu (mm-1)	0.089	0.089
F000	252.0	252.0
F000'	252.12	
h,k,lmax	11,9,14	11,9,14

Nref	1611	1611
Tmin,Tmax	0.981,0.986	0.981,0.986
Tmin'	0.978	

Correction method= # Reported T Limits: Tmin=0.981 Tmax=0.986

AbsCorr = NONE

Data completeness= 1.000 Theta(max)= 28.340

R(reflections)= 0.0607(1172) wR2(reflections)= 0.2048(1603)

S = 1.093 Npar= 103

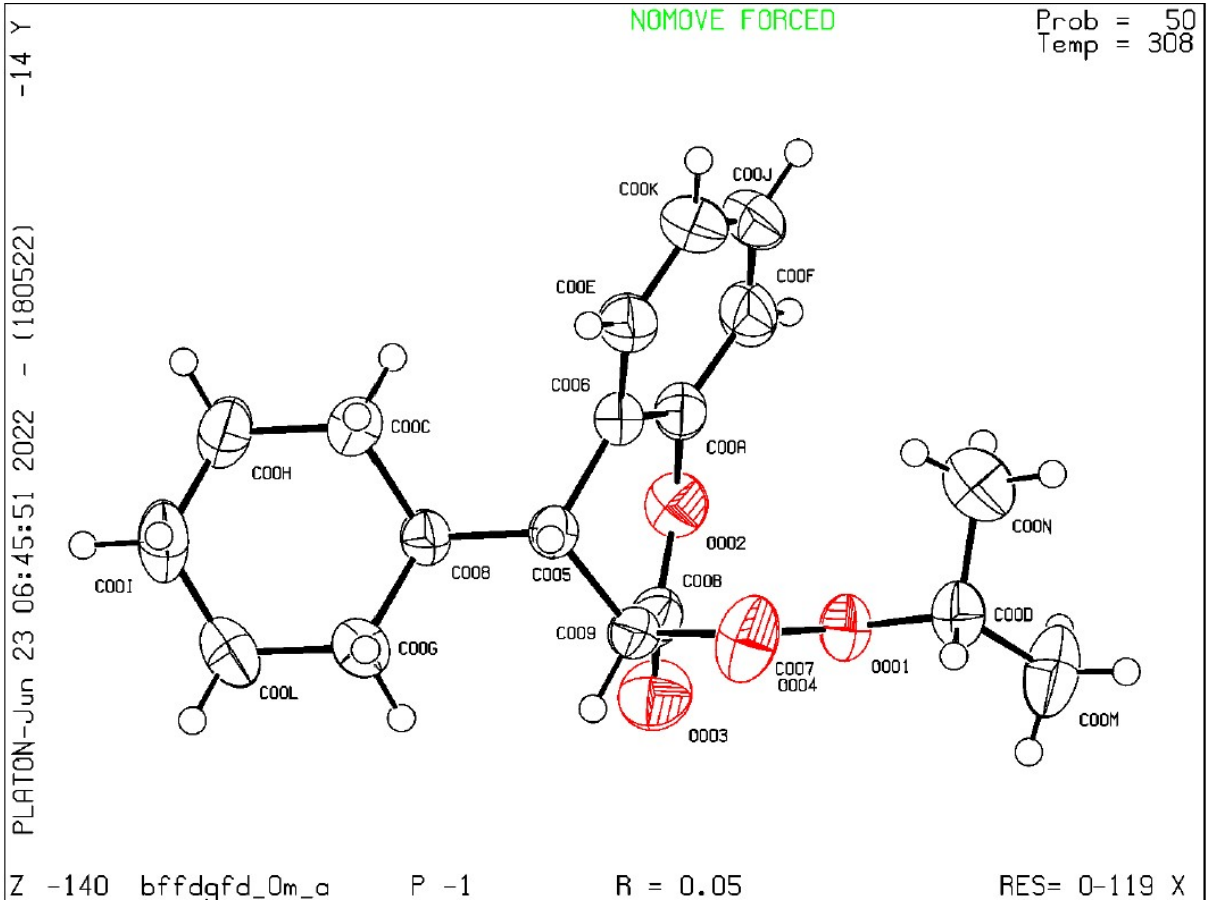


Fig. 2 Single Crystal X-ray Structure of Compound **3t**.

Table S2. Crystal data and structure refinement for 3t

Bond precision: C-C = 0.0021 A Wavelength=0.71073

Cell:	a=9.2320(12)	b=9.6032(13)	c=10.3394(14)
	alpha=75.363(4)	beta=80.372(4)	gamma=79.124(4)
Temperature:	308 K		

	Calculated	Reported
Volume	864.1(2)	864.1(2)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C19 H24 O4	C19 H24 O4
Sum formula	C19 H24 O4	C19 H24 O4
Mr	316.38	316.38
Dx,g cm-3	1.216	1.216
Z	2	2
Mu (mm-1)	0.084	0.084
F000	340.0	340.0
F000’	340.17	
h,k,lmax	12,12,13	12,12,13
Nref	4347	4347
Tmin,Tmax		
Tmin’		

Correction method= Not given

Data completeness= 1.000 Theta(max)= 28.422

R(reflections)= 0.0454(3112) wR2(reflections)= 0.1762(4347)

S = 1.187 Npar= 210

7. References

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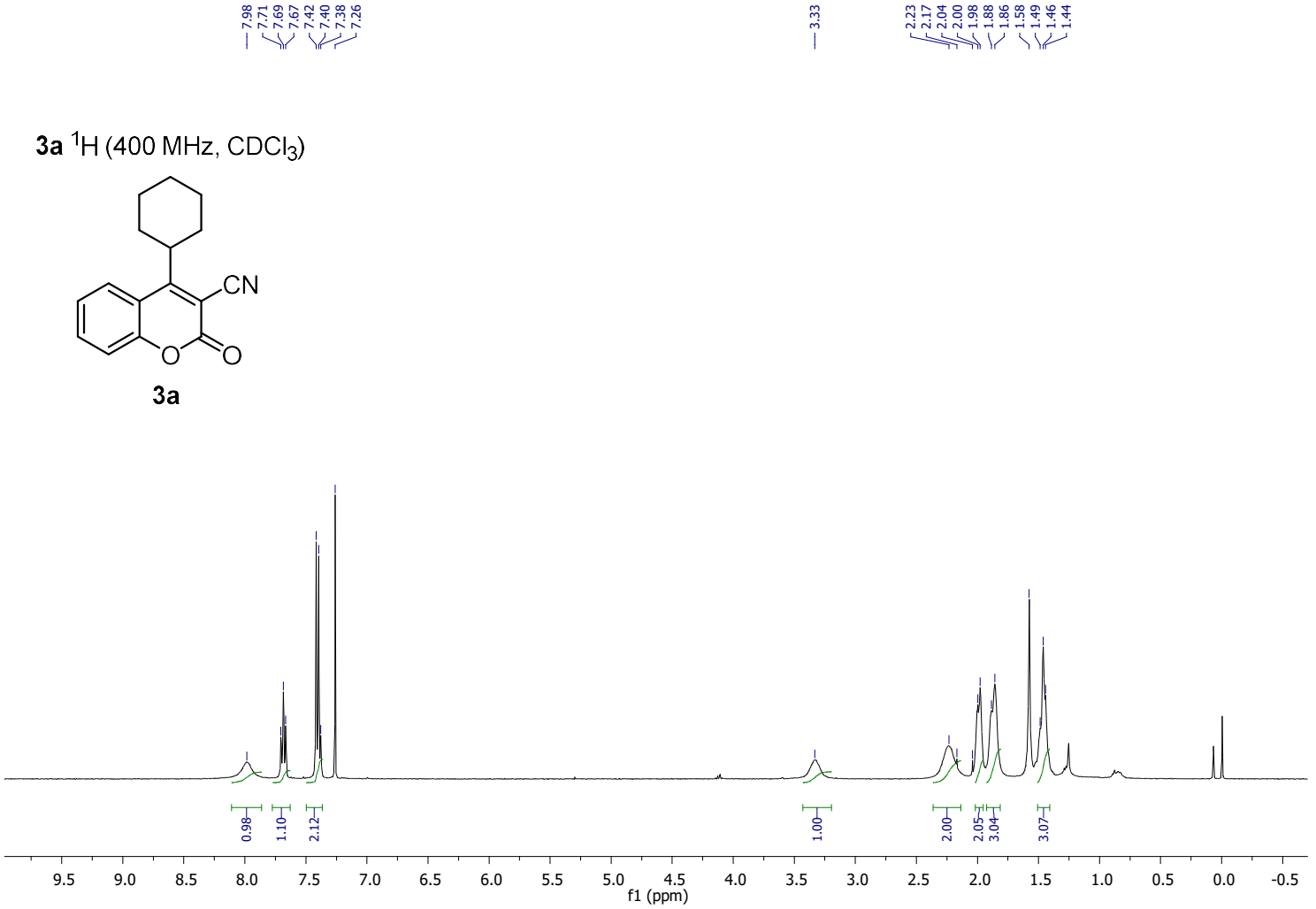
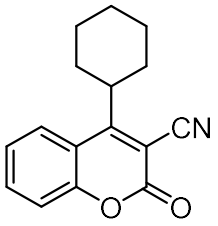
8. ^{1}H and ^{13}C spectra of compounds

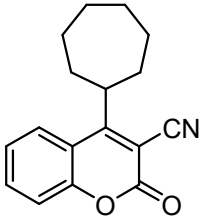


3a ^{13}C {^{1}H} (75 MHz, $CDCl_3$)

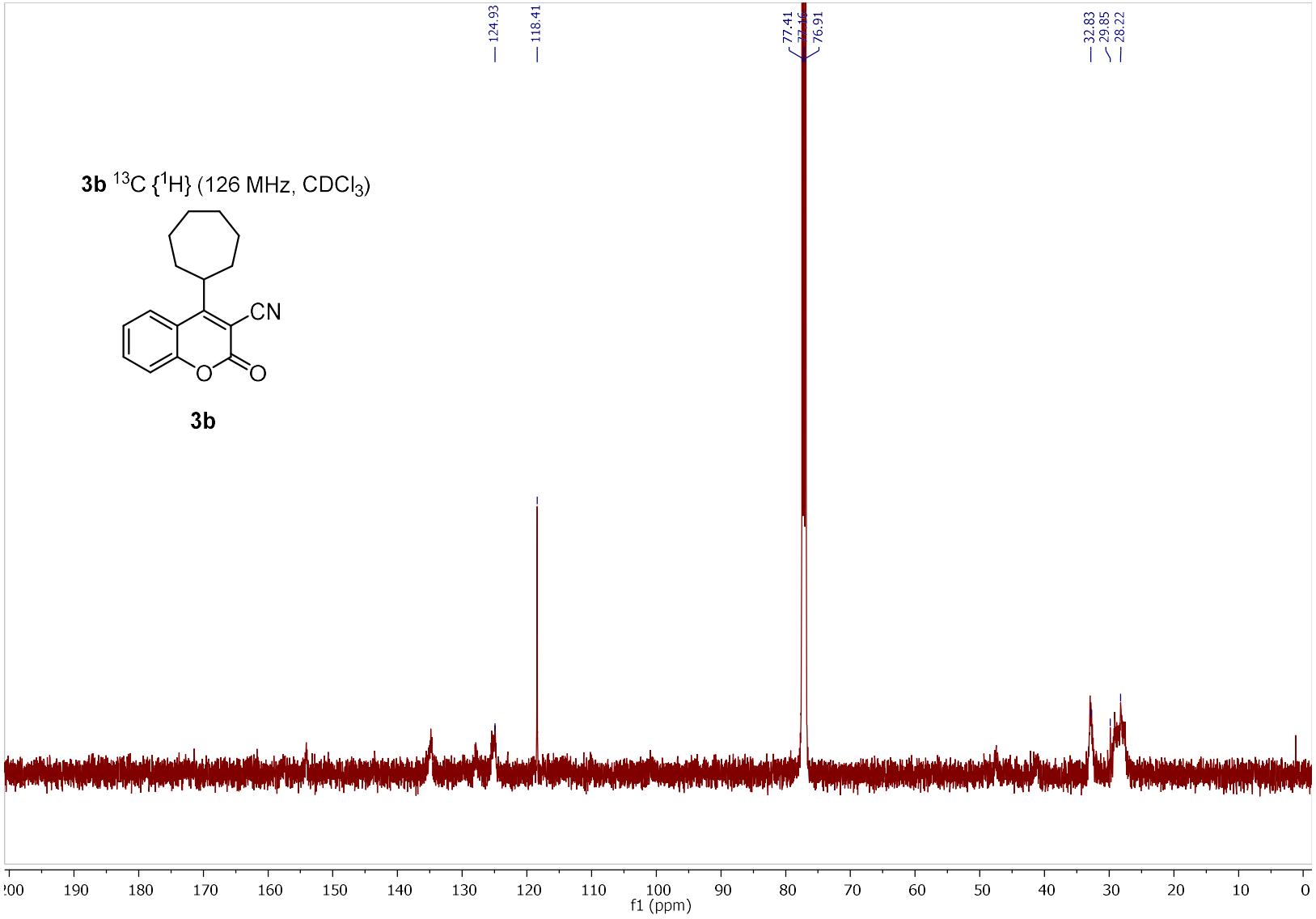


3a

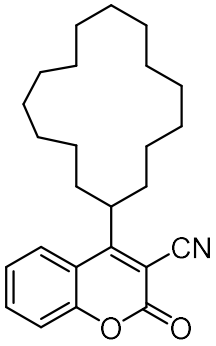
3b ^{1}H (500 MHz, $CDCl_3$)



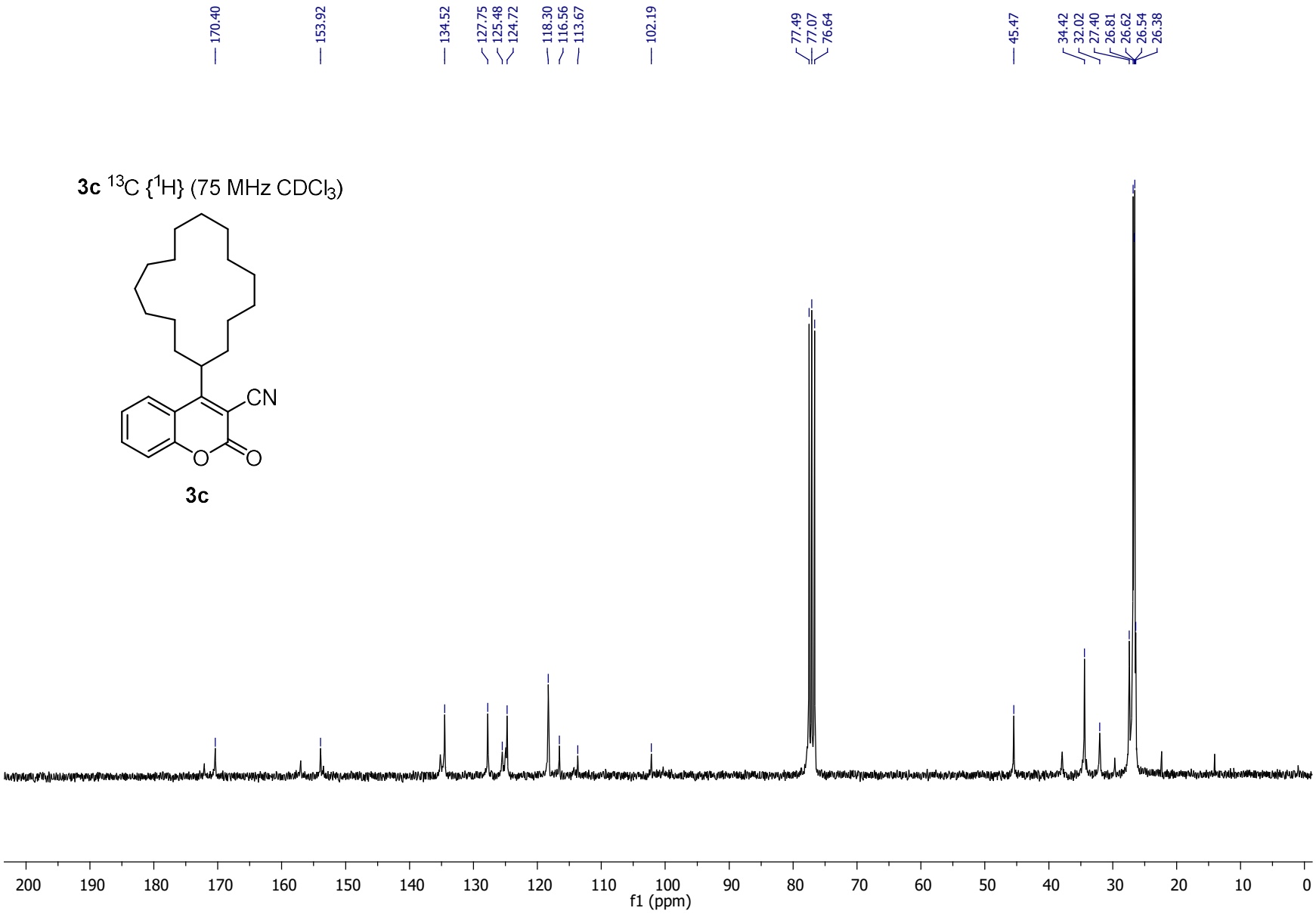
3b


124.93
118.41
77.41
77.16
76.91
32.83
29.85
28.22
3b ^{13}C {^{1}H} (126 MHz, $CDCl_3$)
CN
O
O
3b
f1 (ppm)

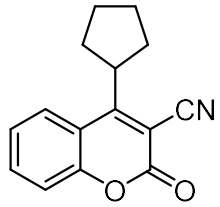
3c ^{1}H (300 MHz $CDCl_3$)



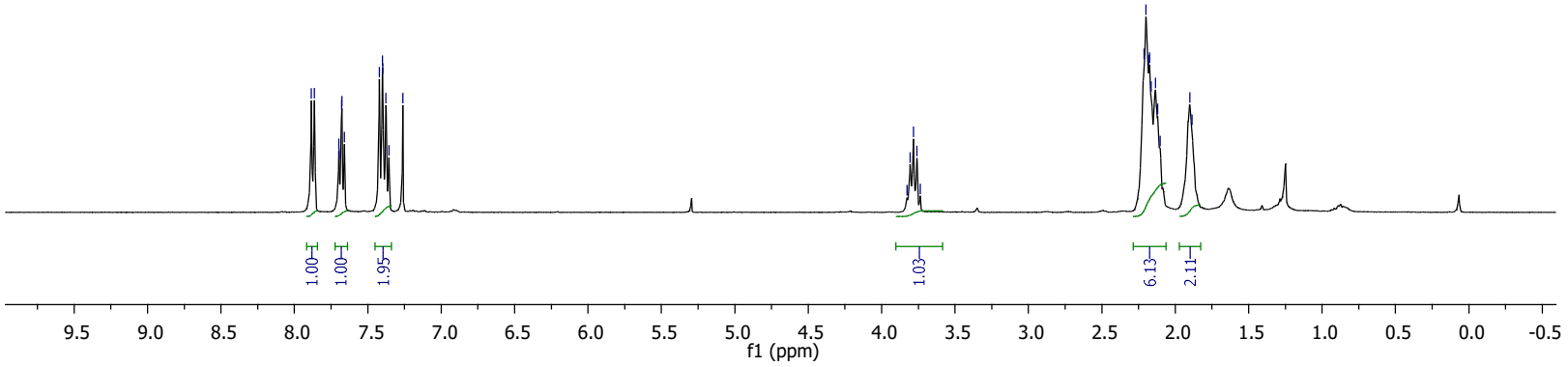
3c


170.40
153.92
134.52
127.75
125.48
124.72
118.30
116.56
113.67
102.19
77.49
77.07
76.64
45.47
34.42
32.02
27.40
26.81
26.62
26.54
26.38
3c ^{13}C {^{1}H} (75 MHz $CDCl_3$)
CN
O
O
3c
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

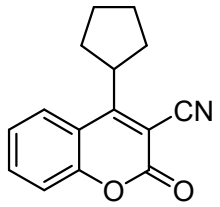
3d ^{1}H (300 MHz, $CDCl_3$)



3d

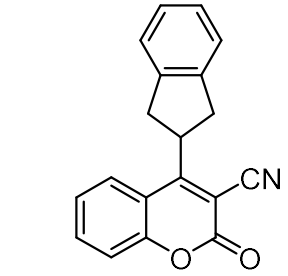


3d $^{13}C\{^{1}H\}$ (75 MHz, $CDCl_3$)

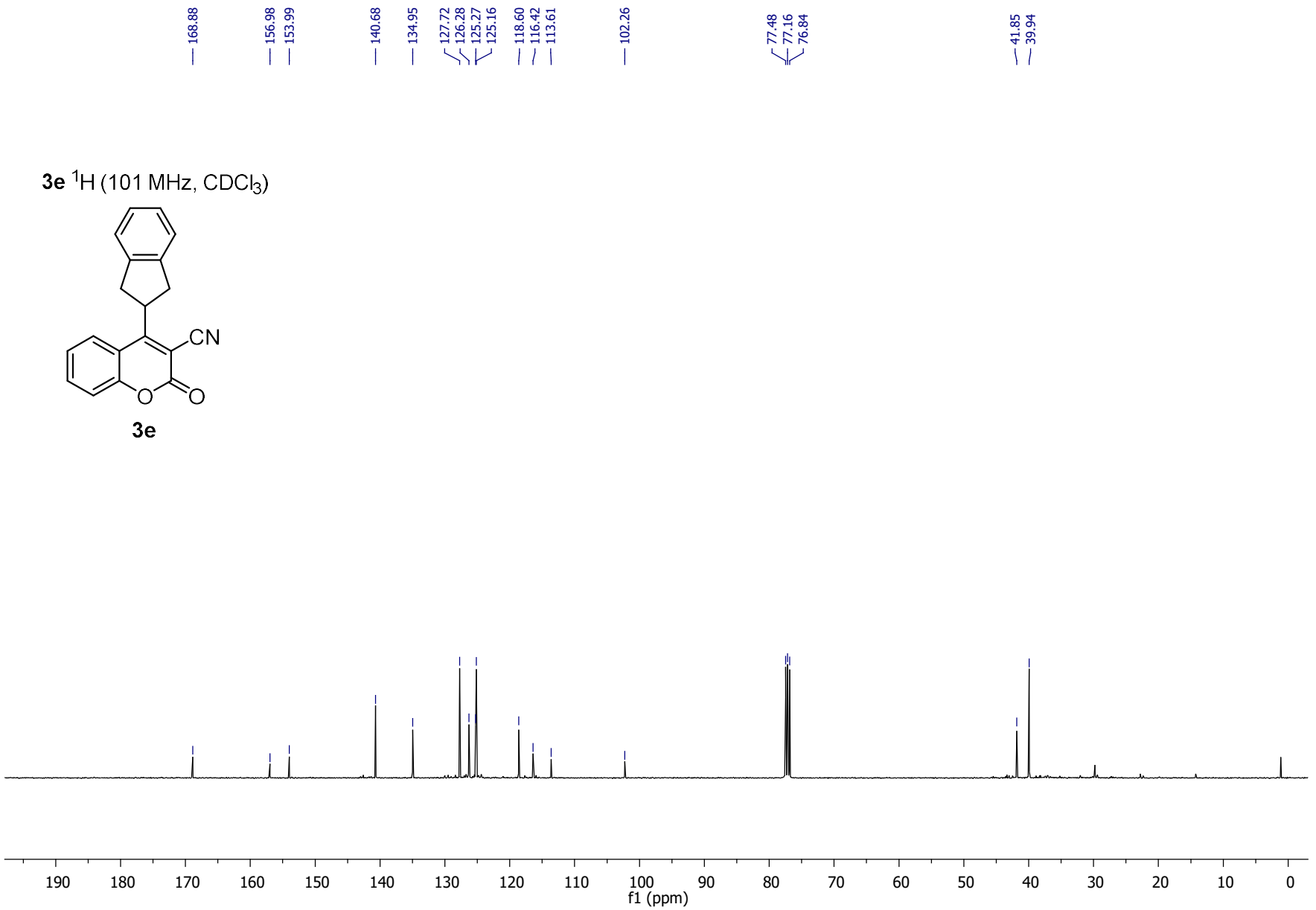


3d

3e ^{1}H (500 MHz, $CDCl_3$)

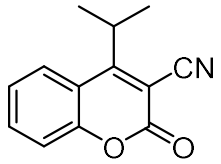


3e

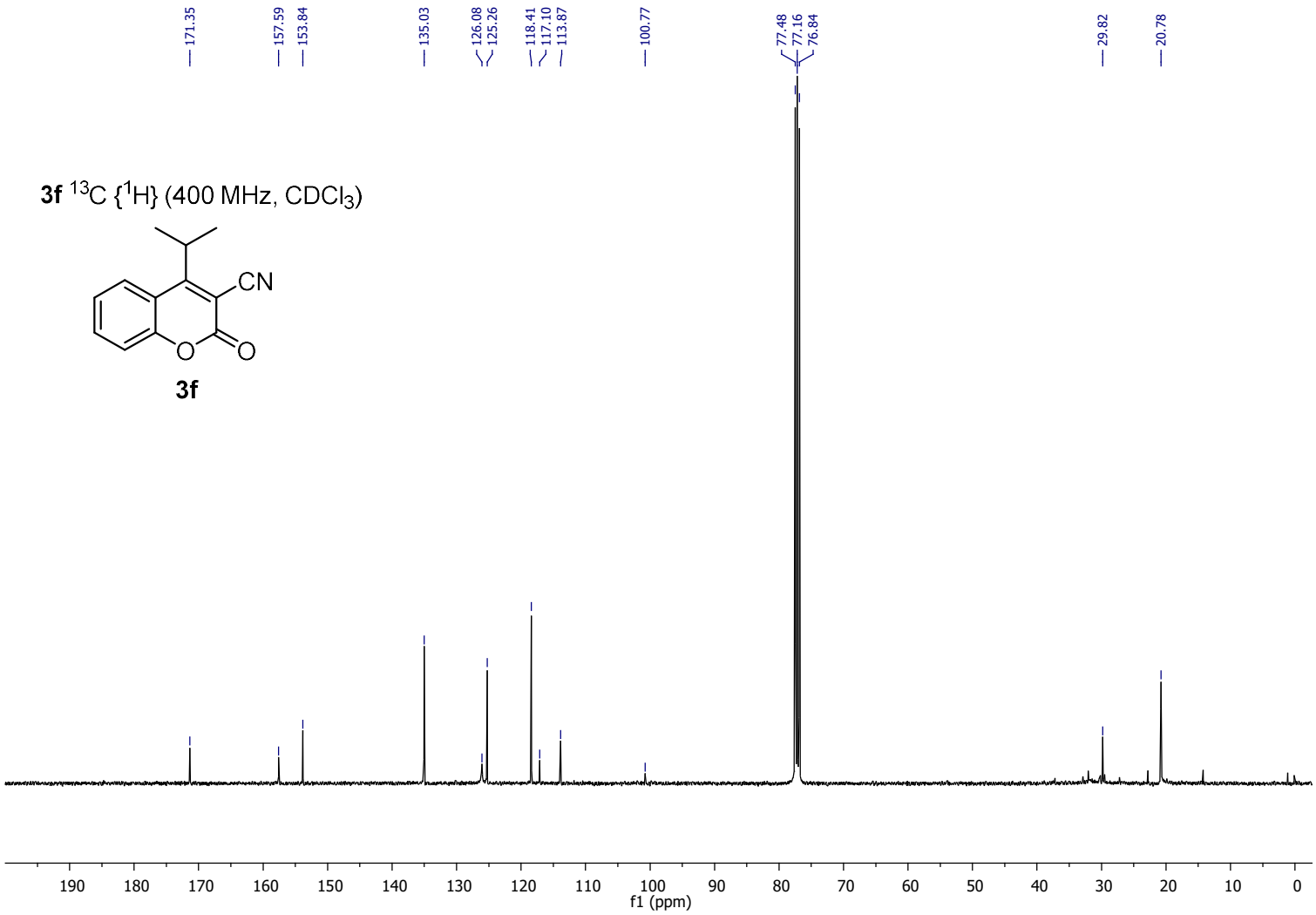


3e ^{1}H (101 MHz, $CDCl_3$)

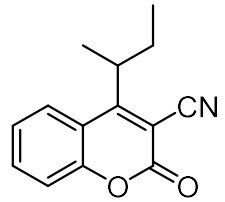
3f ^{1}H (400 MHz, $CDCl_3$)



3f

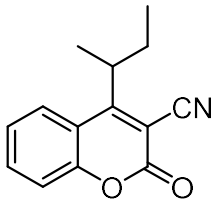

171.35
157.59
153.84
135.03
126.08
125.26
118.41
117.10
113.87
100.77
77.48
77.16
76.84
29.82
20.78
3f ^{13}C {^{1}H} (400 MHz, $CDCl_3$)
CN
O
O
3f
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3g ^{1}H (500 MHz, $CDCl_3$)

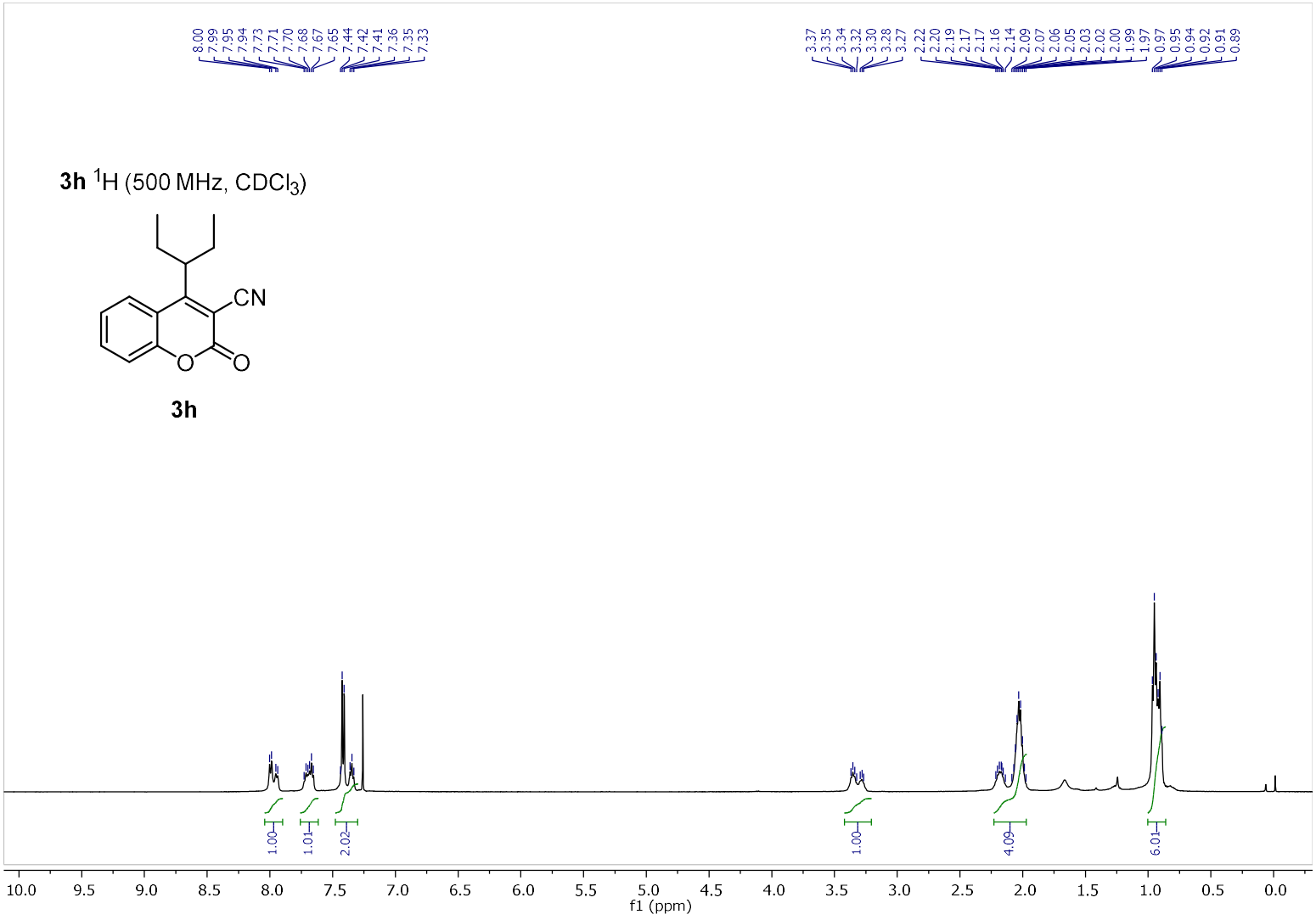


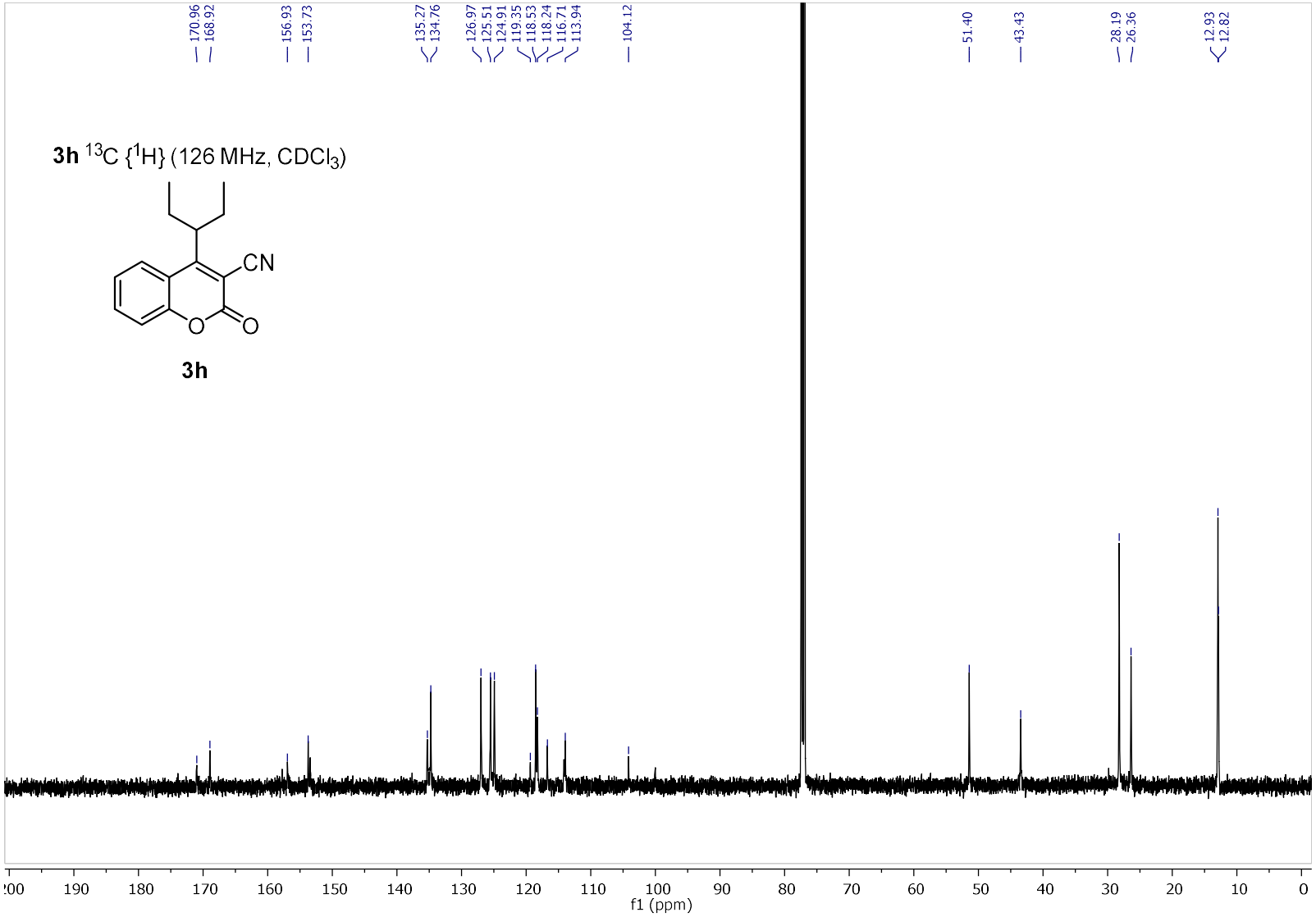
3g

3g ^{13}C {^{1}H} (500 MHz, $CDCl_3$)

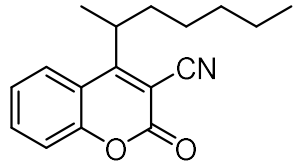


3g


8.00
7.99
7.95
7.94
7.73
7.71
7.70
7.68
7.67
7.65
7.44
7.42
7.41
7.36
7.35
7.33
3.37
3.35
3.34
3.32
3.30
3.28
3.27
2.22
2.20
2.19
2.17
2.17
2.16
2.14
2.09
2.07
2.06
2.05
2.03
2.02
2.00
1.99
1.97
0.97
0.95
0.94
0.92
0.91
0.89
3h ^{1}H (500 MHz, $CDCl_3$)
CN
O
O
3h
1.00
1.01
2.02
1.00
4.09
6.01
10.0
9.5
9.0
8.5
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
1.5
1.0
0.5
0.0
f1 (ppm)

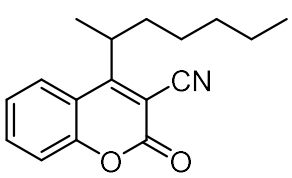

3h $^{13}C\{^{1}H\}$ (126 MHz, $CDCl_3$)
CN
O
O
3h
170.96
168.92
156.93
153.73
135.27
134.76
126.97
125.51
124.91
119.35
118.53
118.24
116.71
113.94
104.12
51.40
43.43
28.19
26.36
12.93
12.82
f1 (ppm)

3i ^{1}H (500 MHz, $CDCl_3$)



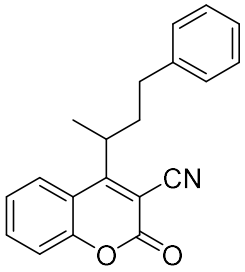
3i

3i $^{13}C\{^{1}H\}$ (75 MHz, $CDCl_3$)

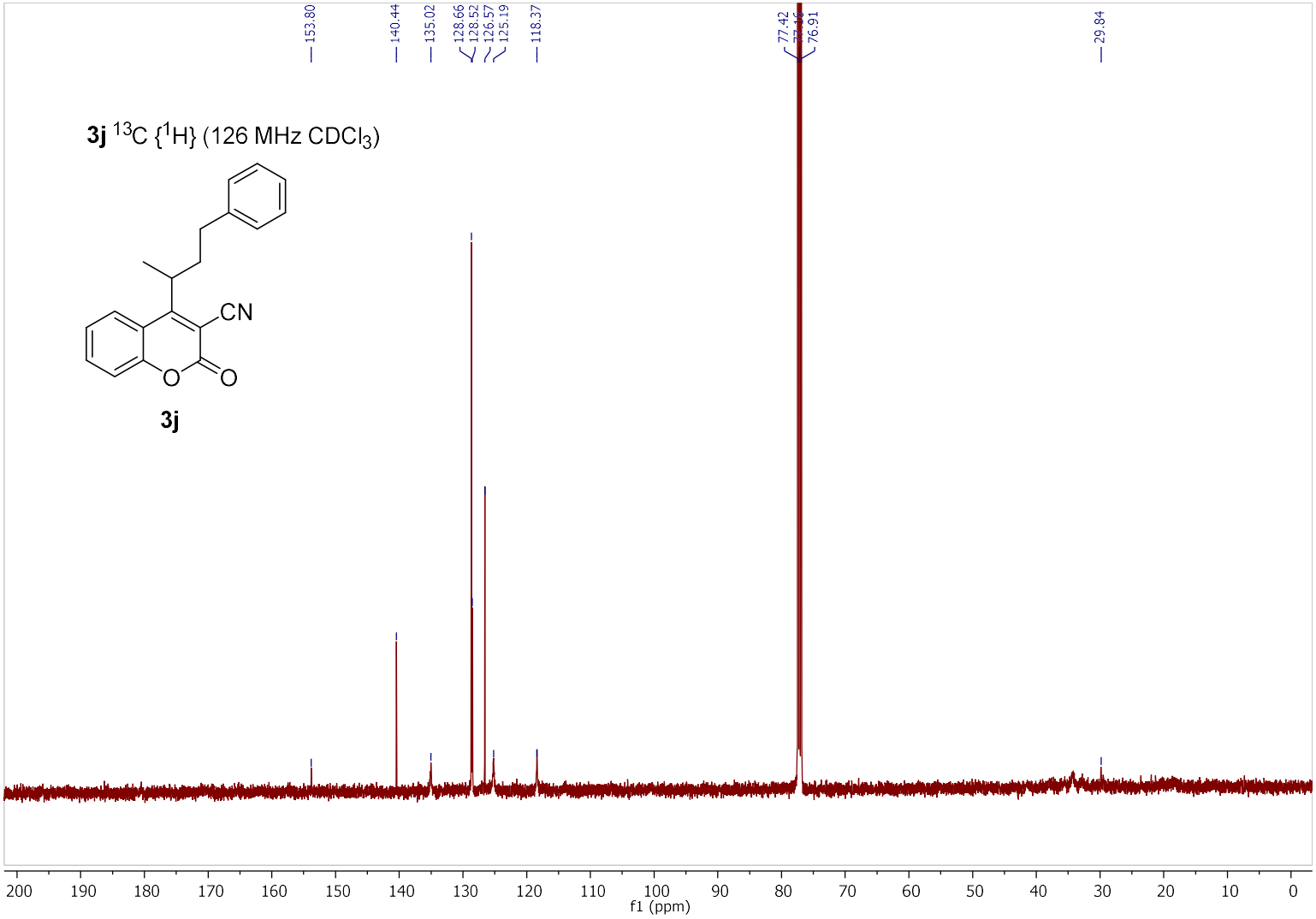


3i

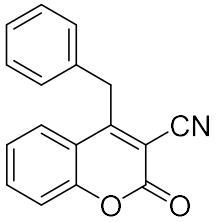
3j ^{1}H (400 MHz $CDCl_3$)



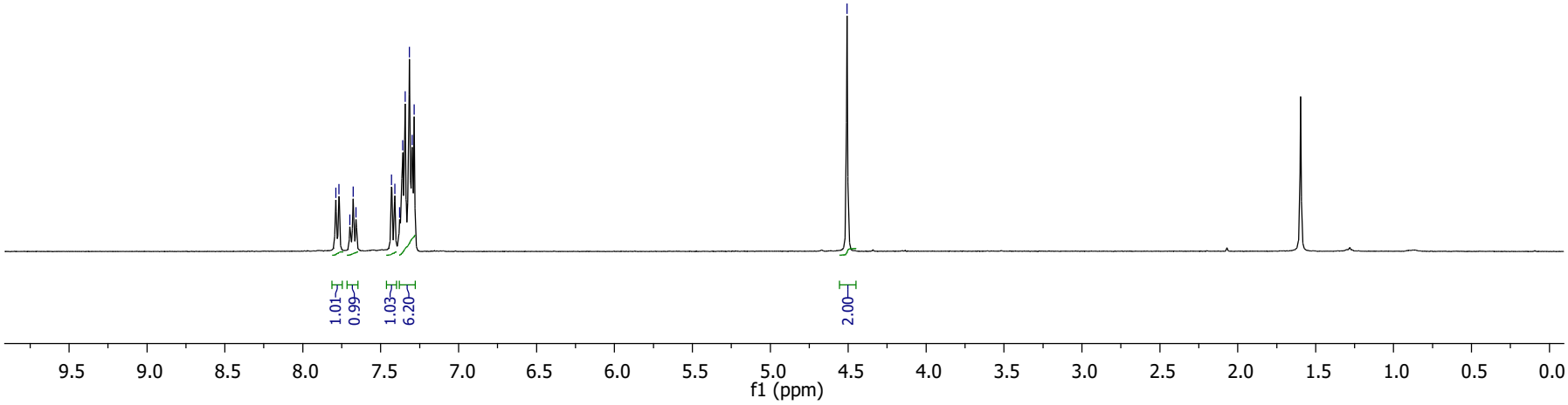
3j


153.80
140.44
135.02
128.66
128.52
126.57
125.19
118.37
77.42
77.16
76.91
29.84
3j ^{13}C {^{1}H} (126 MHz $CDCl_3$)
CN
O
O
3j
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

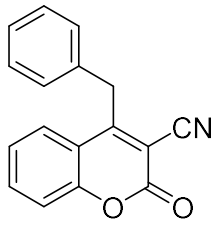
3k ^{1}H (400 MHz $CDCl_3$)



3k

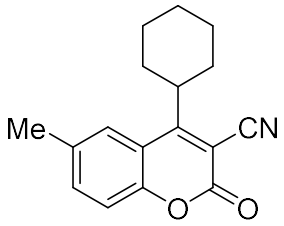


3k ^{13}C {^{1}H} (101 MHz $CDCl_3$)



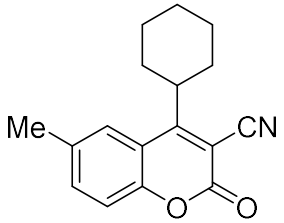
3k

3l ^{1}H (400 MHz $CDCl_3$)



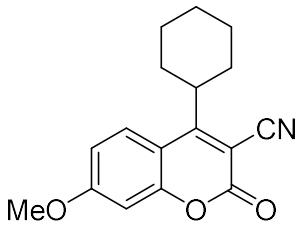
3l

3l ^{13}C {1H} (75 MHz $CDCl_3$)

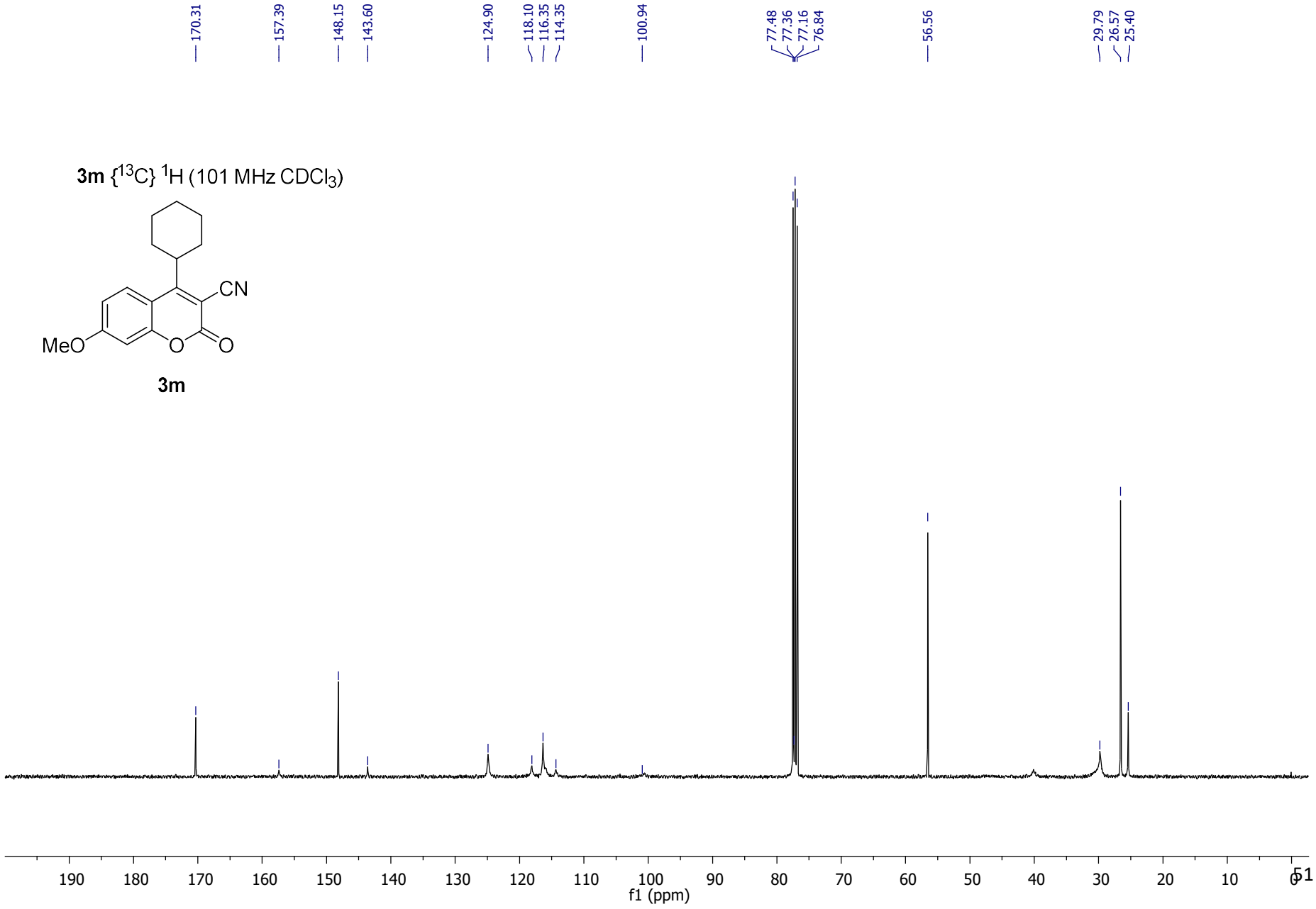


3l

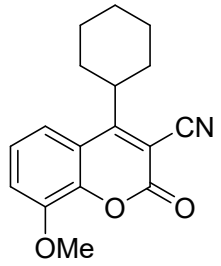
3m ^{1}H (400 MHz $CDCl_3$)



3m

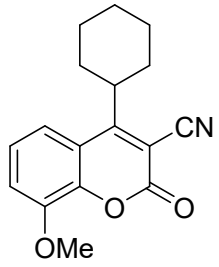

170.31
157.39
148.15
143.60
124.90
118.10
116.35
114.35
100.94
77.48
77.36
77.16
76.84
56.56
29.79
26.57
25.40
3m {13C} 1H (101 MHz CDCl3)
CN
MeO
O
O
3m
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3n ^{1}H (400 MHz $CDCl_3$)

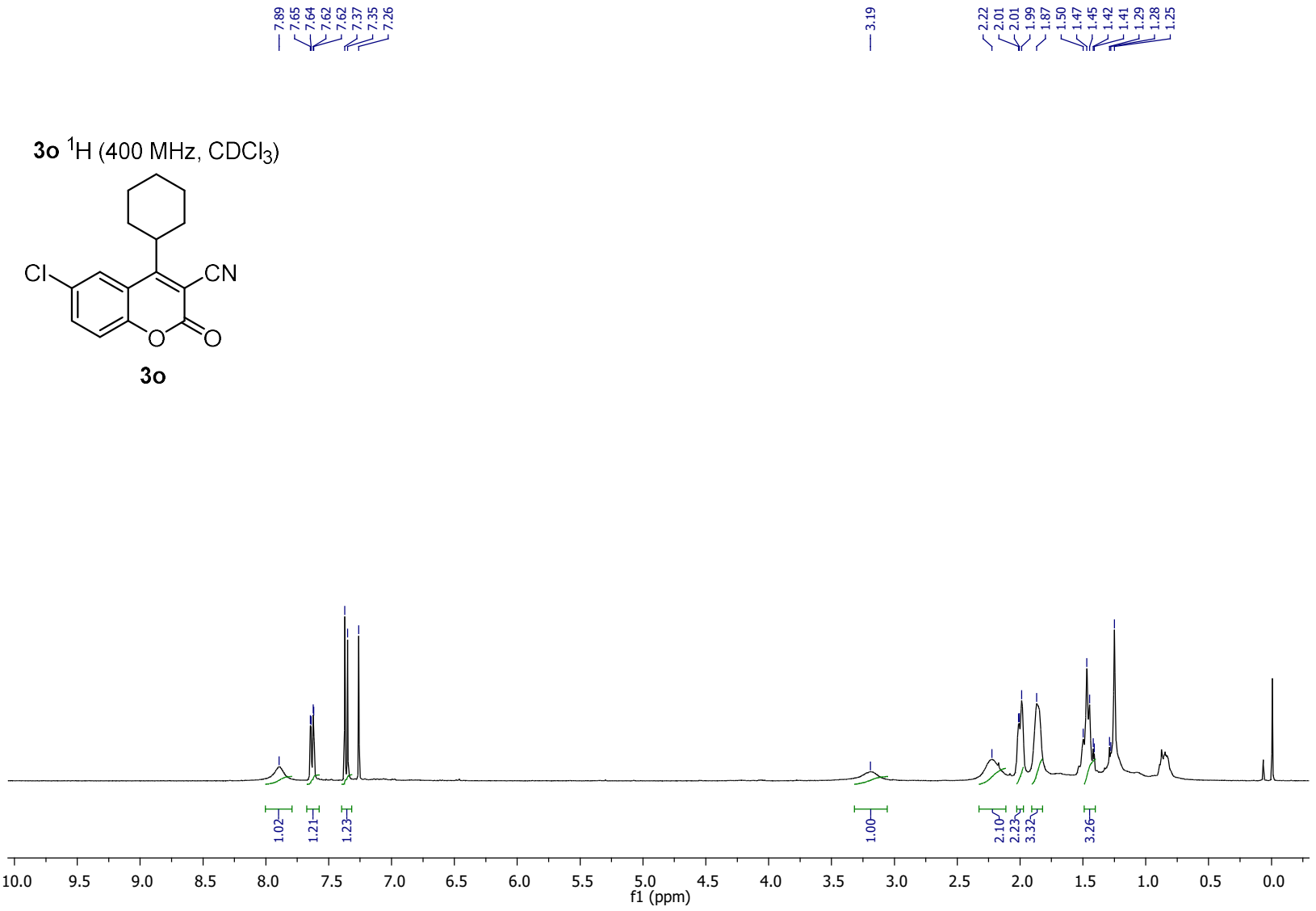


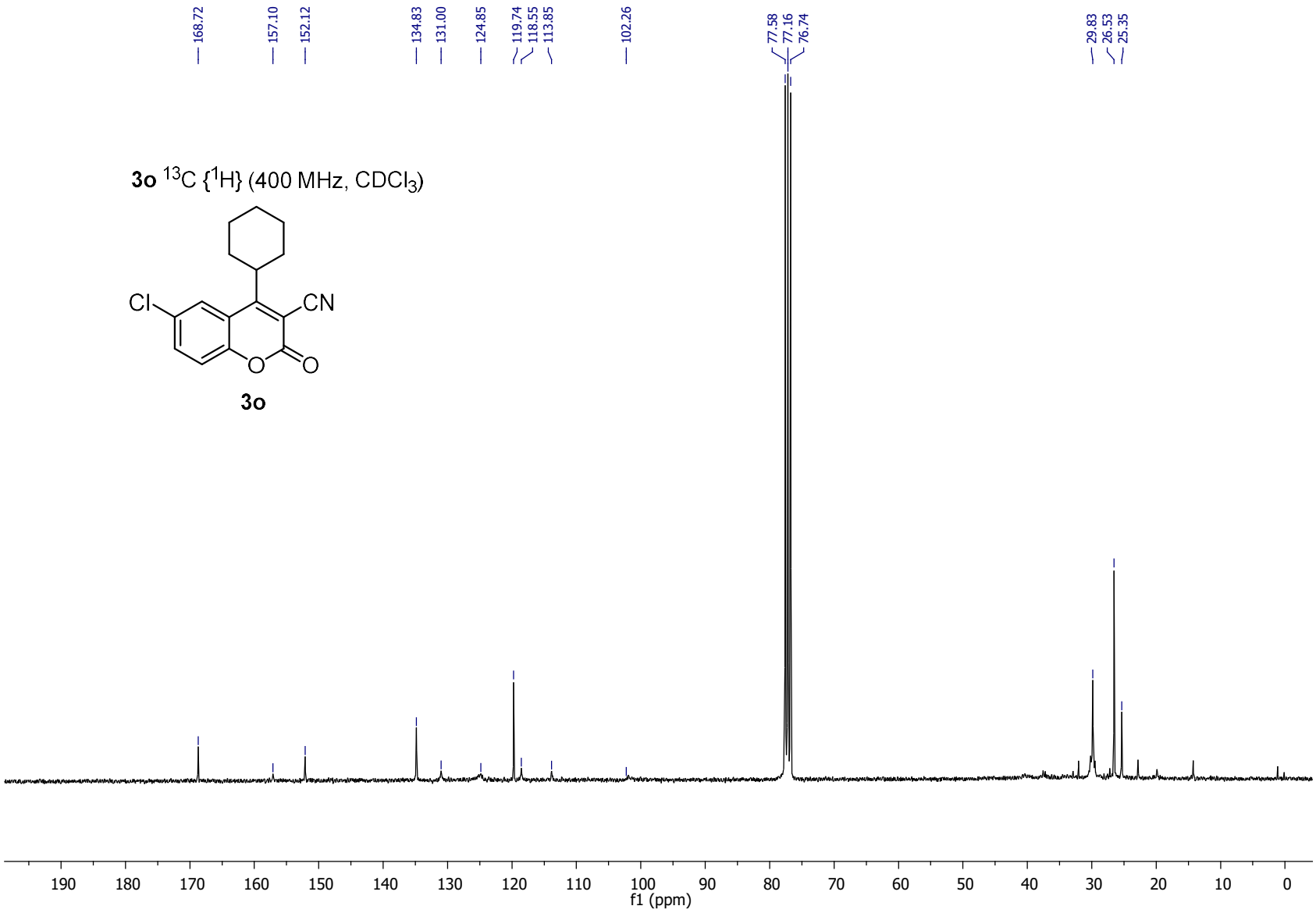
3n

3n ^{13}C {^{1}H} (101 MHz $CDCl_3$)

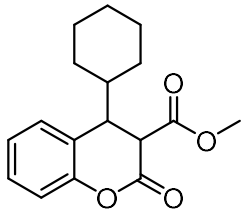


3n

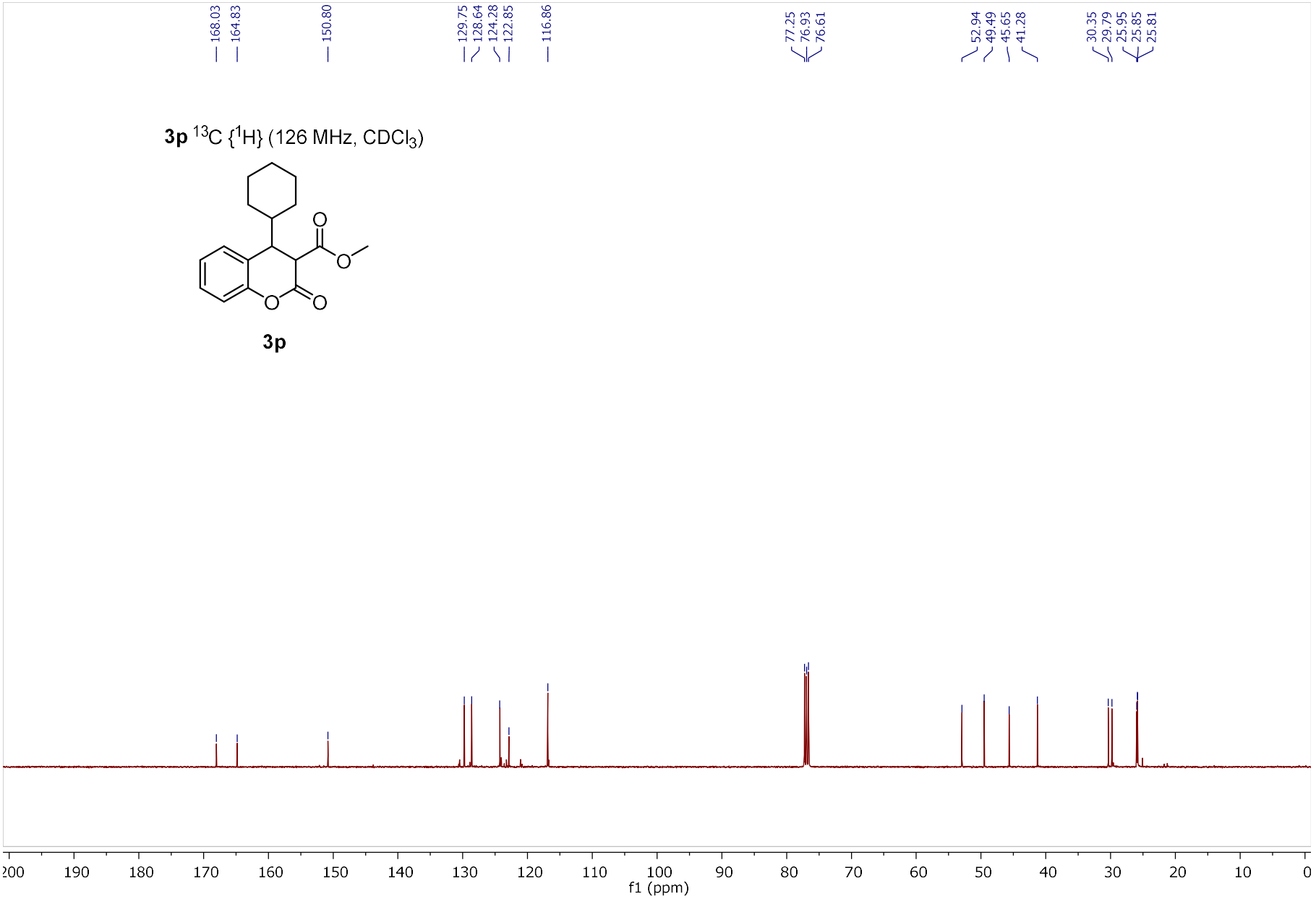

7.89
7.65
7.64
7.62
7.62
7.37
7.35
7.26
3.19
2.22
2.01
2.01
1.99
1.87
1.50
1.47
1.45
1.42
1.41
1.29
1.28
1.25
3o ^{1}H (400 MHz, $CDCl_3$)
Cl
CN
O
O
3o
1.02
1.21
1.23
1.00
2.10
2.23
3.32
3.26
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


168.72
157.10
152.12
134.83
131.00
124.85
119.74
118.55
113.85
102.26
77.58
77.16
76.74
29.83
26.53
25.35
3o ^{13}C {^{1}H} (400 MHz, $CDCl_3$)
Cl
CN
O
O
3o
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

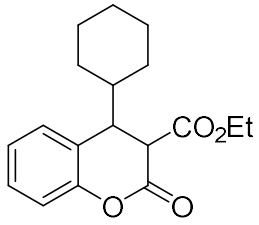
3p ^{1}H (500 MHz, $CDCl_3$)



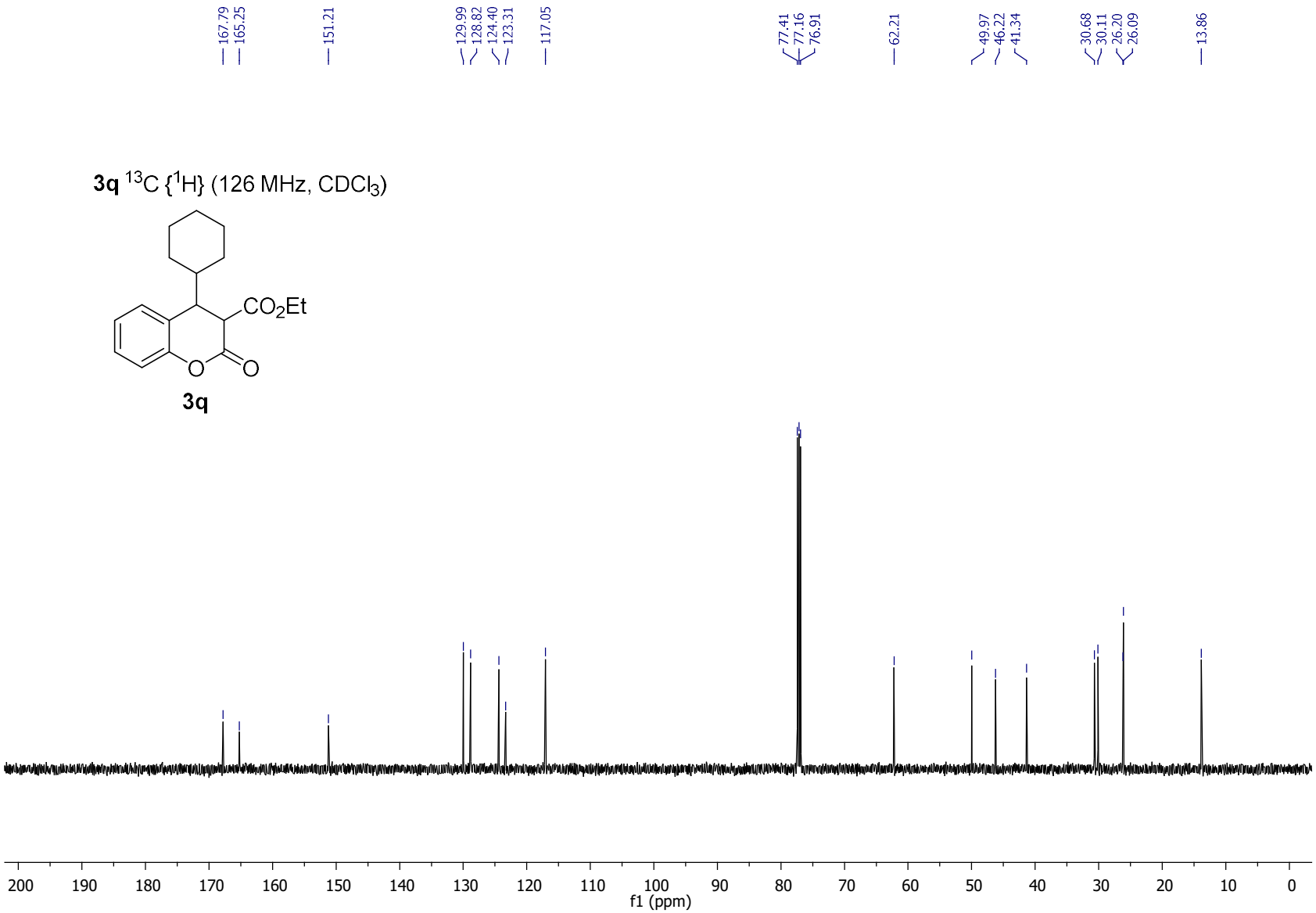
3p

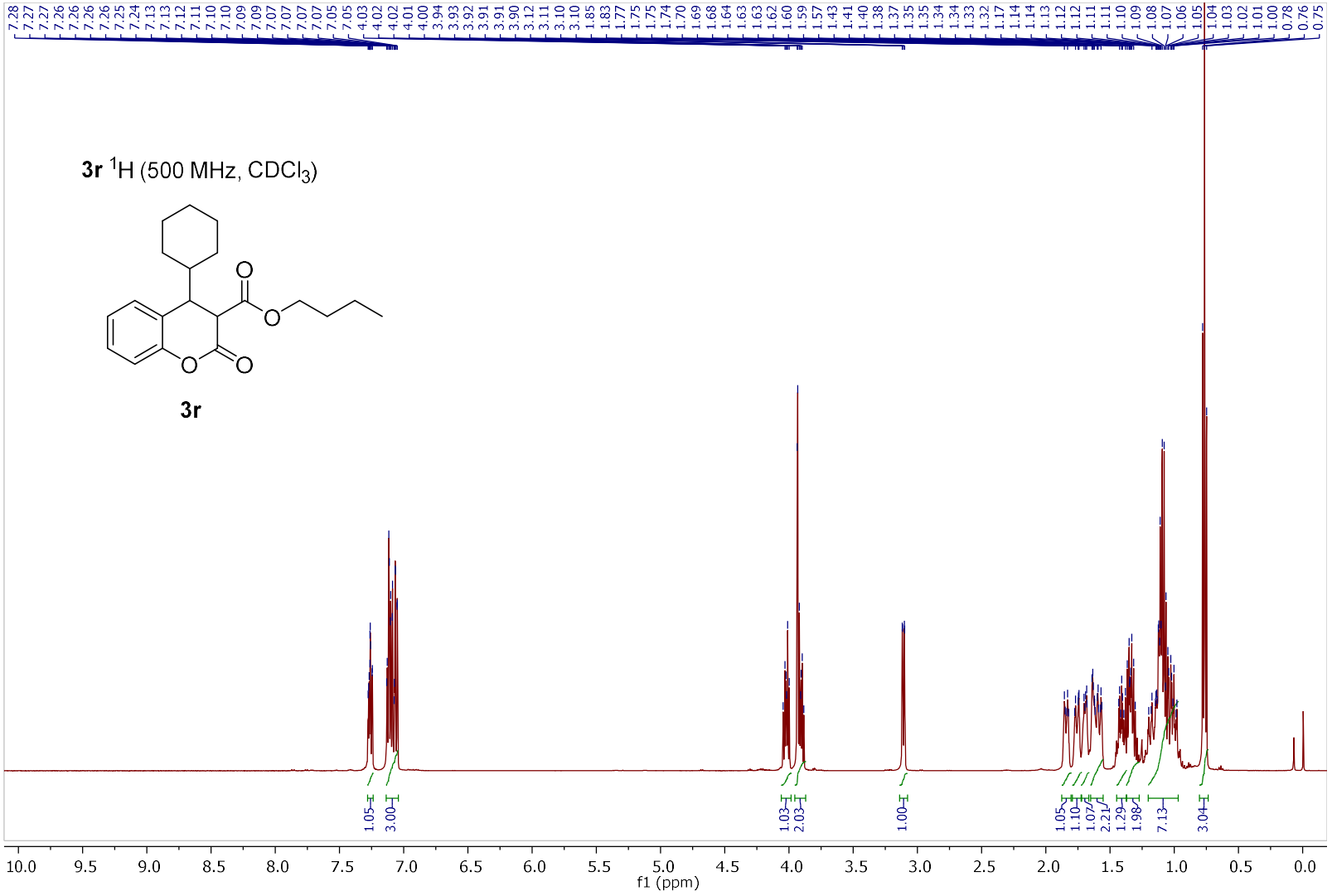

168.03
164.83
150.80
129.75
128.64
124.28
122.85
116.86
77.25
76.93
76.61
52.94
49.49
45.65
41.28
30.35
29.79
25.95
25.85
25.81
3p ^{13}C {^{1}H} (126 MHz, $CDCl_3$)
O
O
O
O
3p
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

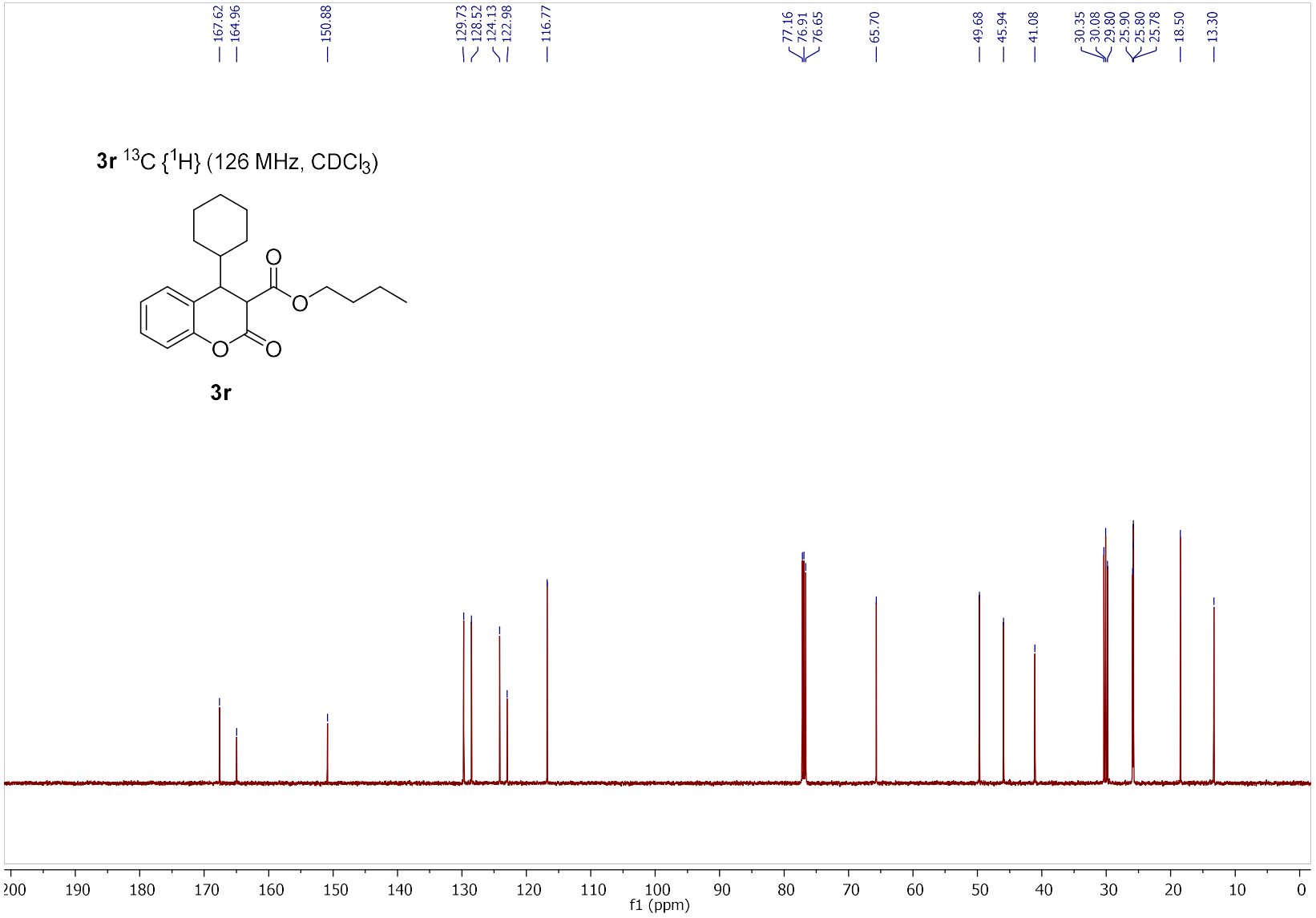
3q ^{1}H (500 MHz, $CDCl_3$)

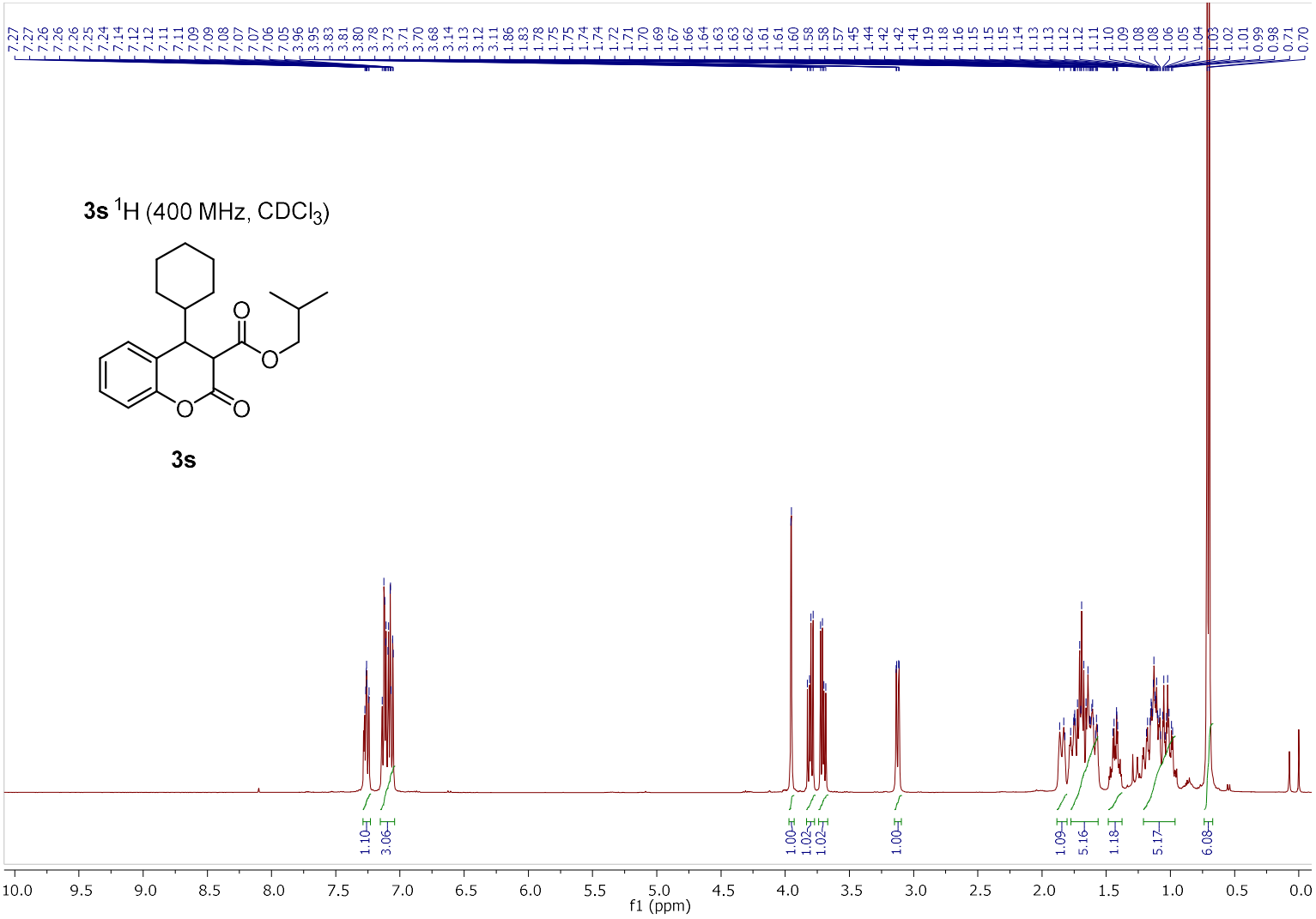


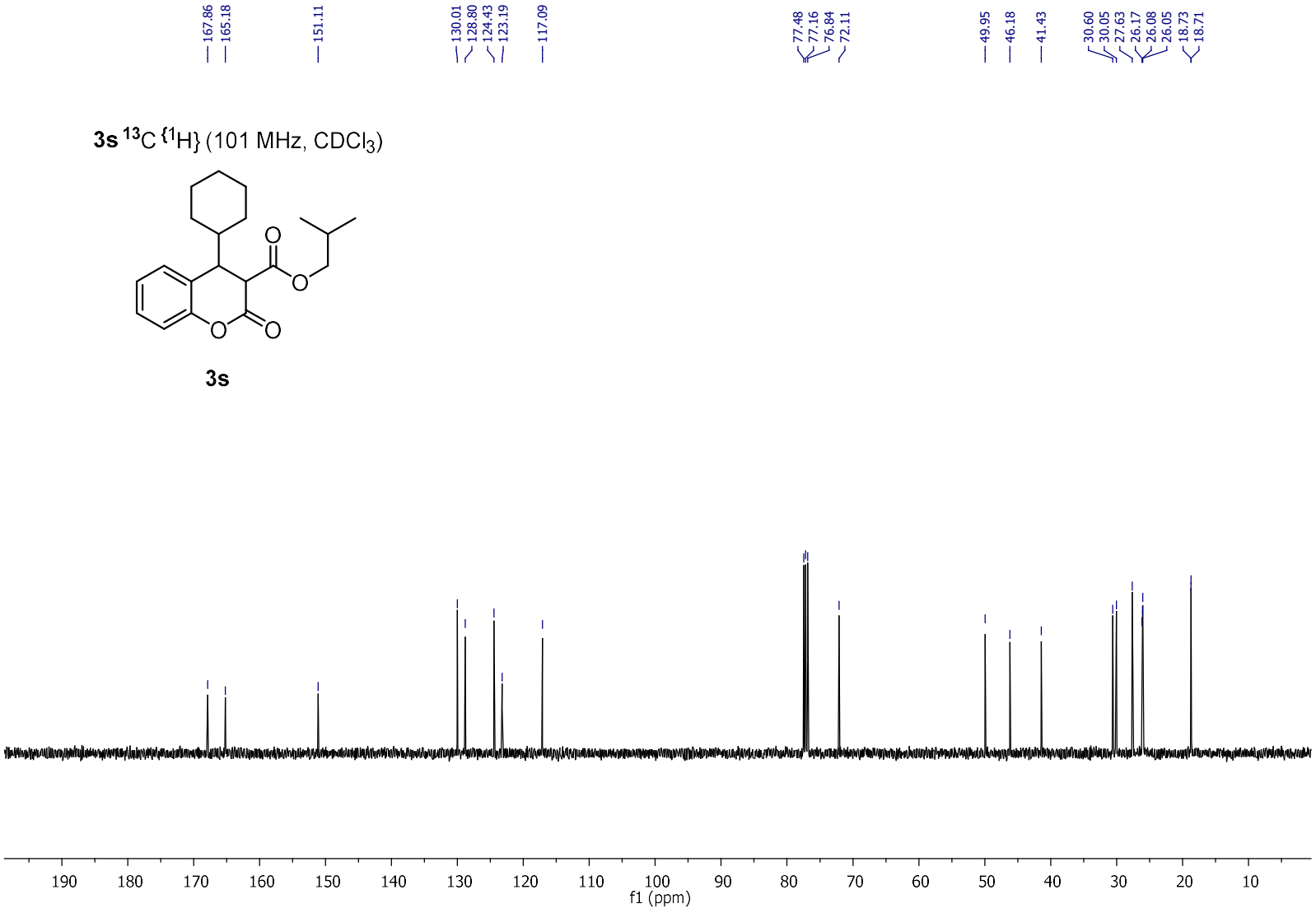
3q


167.79
165.25
151.21
129.99
128.82
124.40
123.31
117.05
77.41
77.16
76.91
62.21
49.97
46.22
41.34
30.68
30.11
26.20
26.09
13.86
3q $^{13}C\{^{1}H\}$ (126 MHz, $CDCl_3$)
CO_2Et
O
O
3q
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

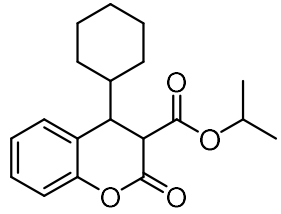

3r ^{1}H (500 MHz, $CDCl_3$)
3r
f1 (ppm)


167.62
164.96
150.88
129.73
128.52
124.13
122.98
116.77
77.16
76.91
76.65
65.70
49.68
45.94
41.08
30.35
30.08
29.80
25.90
25.80
25.78
18.50
13.30
3r $^{13}C\{^{1}H\}$ (126 MHz, $CDCl_3$)
O
O
O
O
3r
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

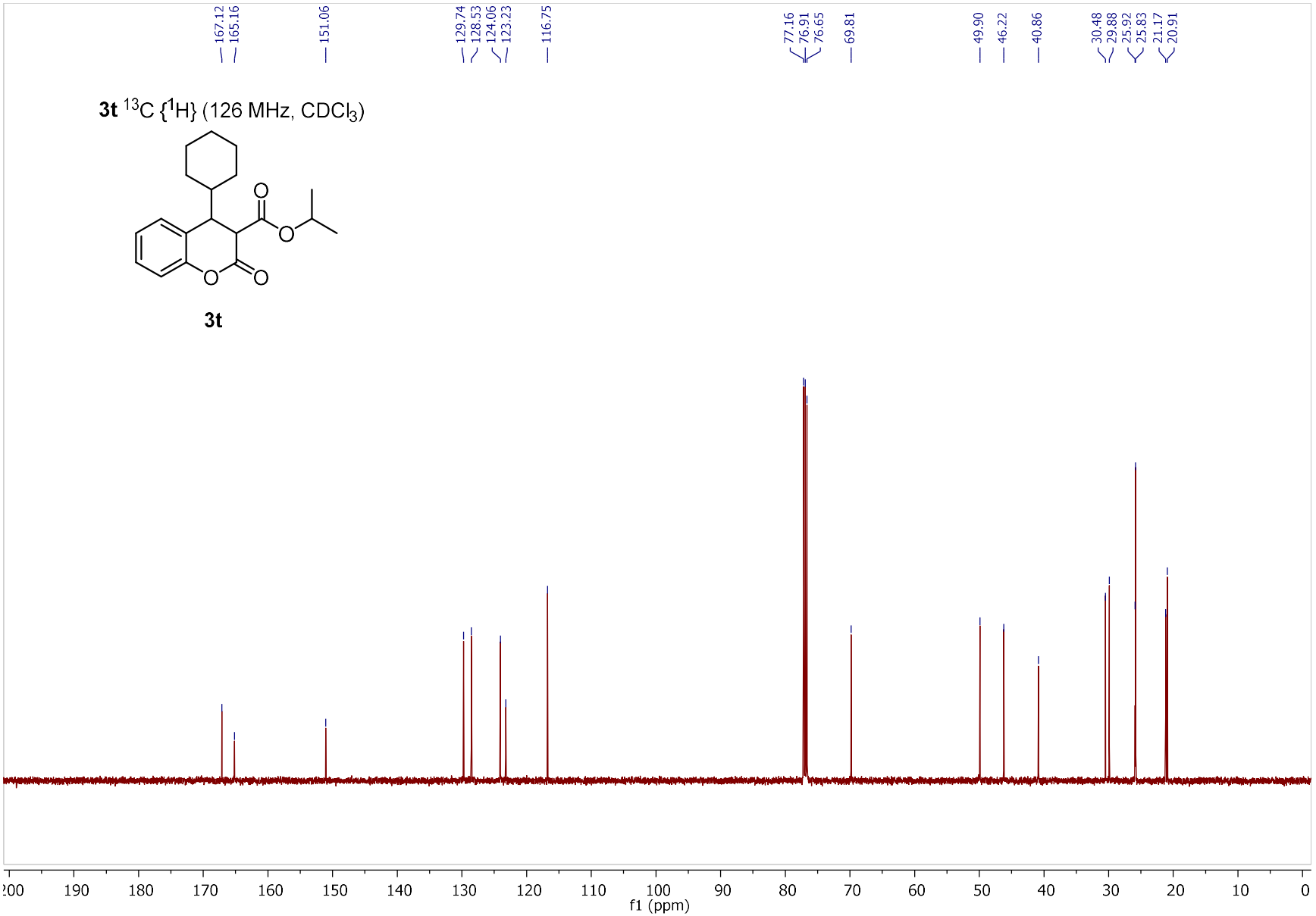

3s ^{1}H (400 MHz, $CDCl_3$)
3s
f1 (ppm)

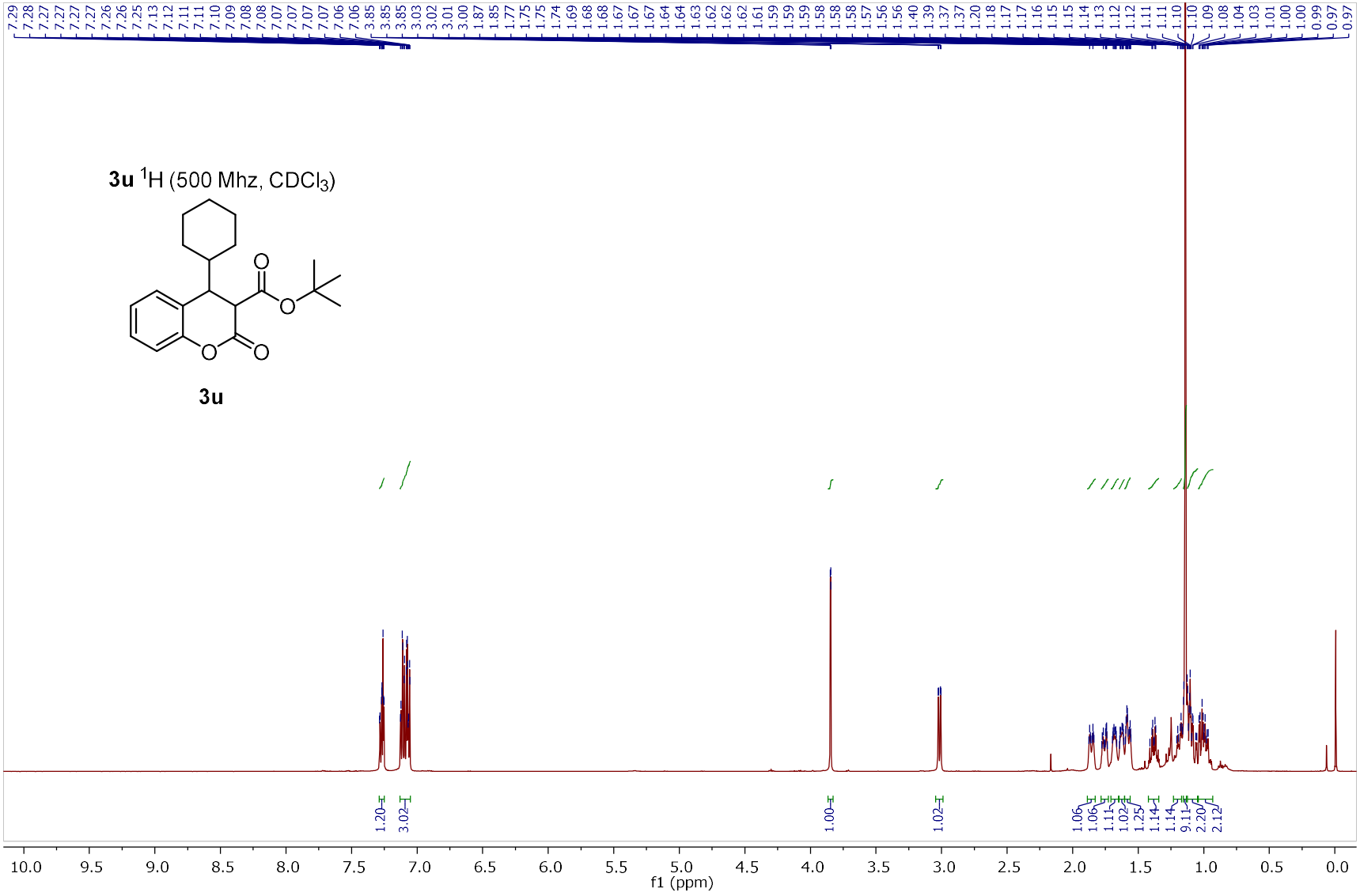

167.86
165.18
151.11
130.01
128.80
124.43
123.19
117.09
77.48
77.16
76.84
72.11
49.95
46.18
41.43
30.60
30.05
27.63
26.17
26.08
26.05
18.73
18.71
3s $^{13}C\{^{1}H\}$ (101 MHz, $CDCl_3$)
3s
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

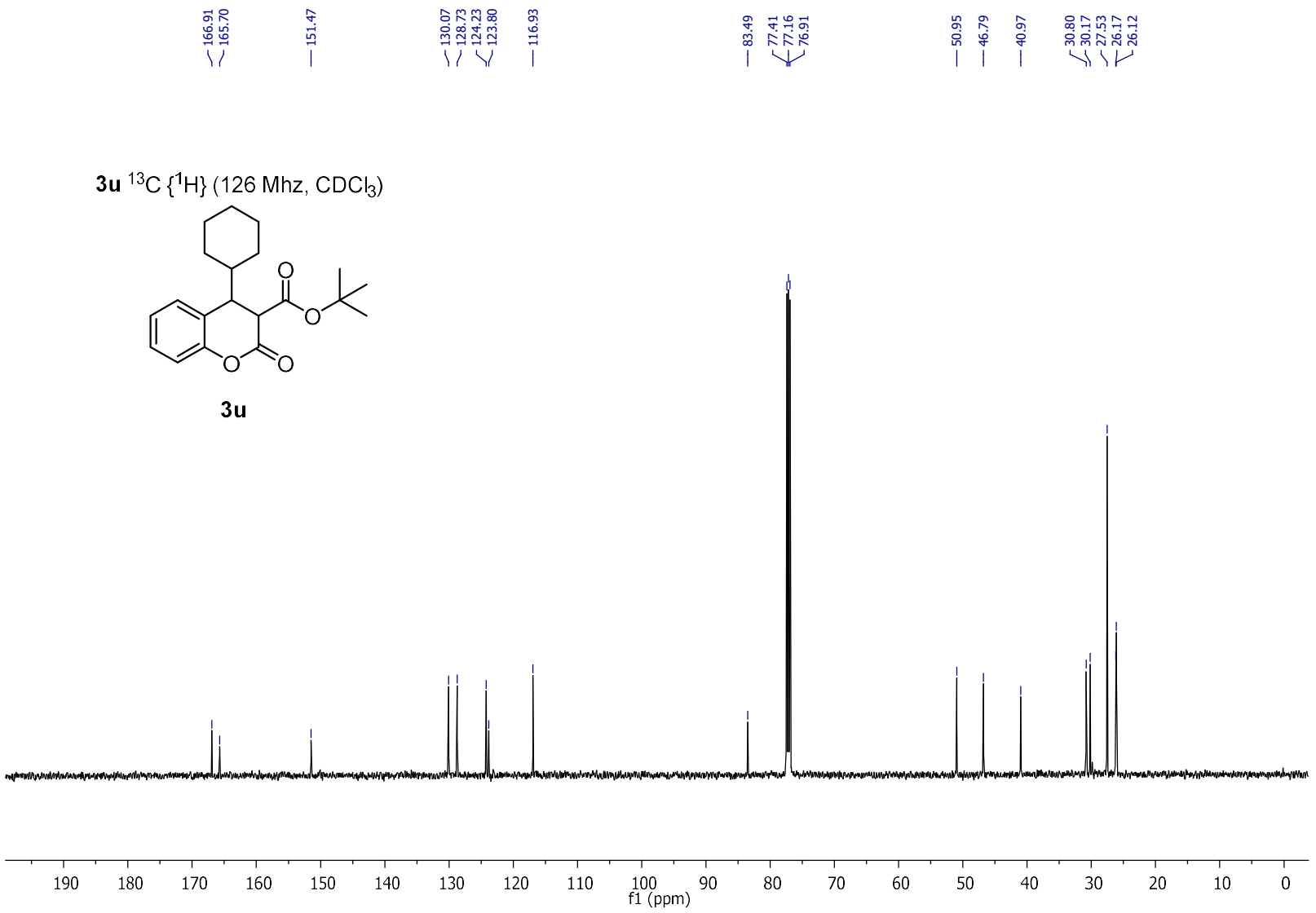
3t ^{1}H (500 MHz, $CDCl_3$)



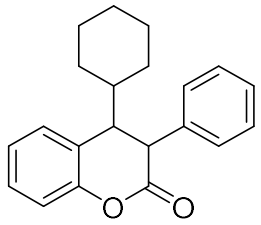
3t


167.12
165.16
151.06
129.74
128.53
124.06
123.23
116.75
77.16
76.91
76.65
69.81
49.90
46.22
40.86
30.48
29.88
25.92
25.83
21.17
20.91
3t $^{13}C\{^{1}H\}$ (126 MHz, $CDCl_3$)
3t
f1 (ppm)

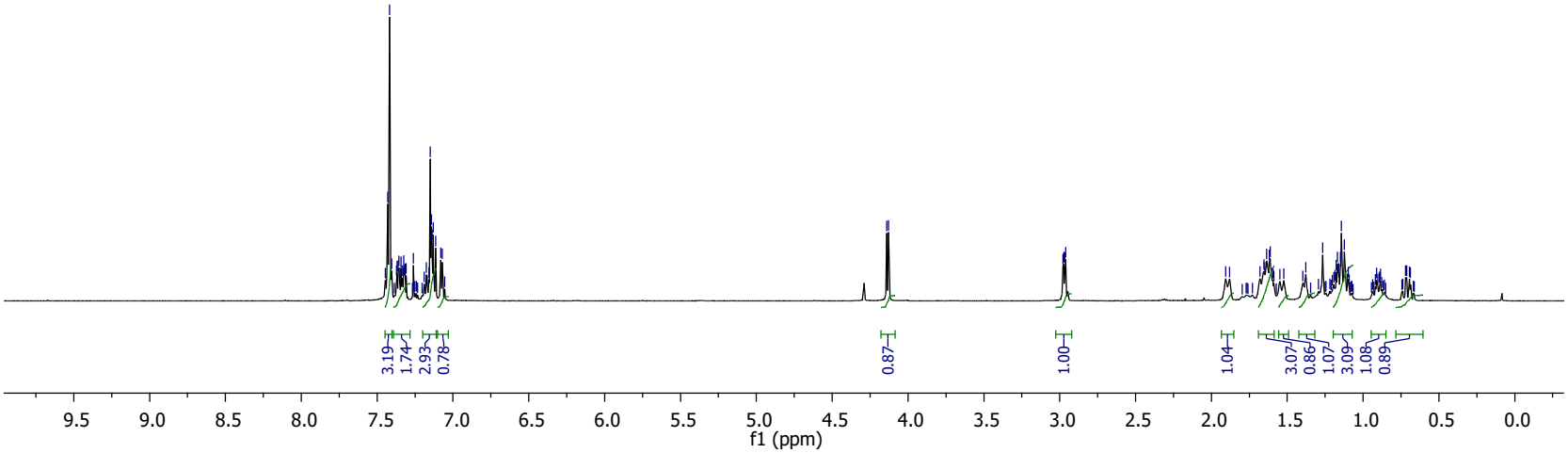

3u ^{1}H (500 Mhz, $CDCl_3$)
3u
f1 (ppm)

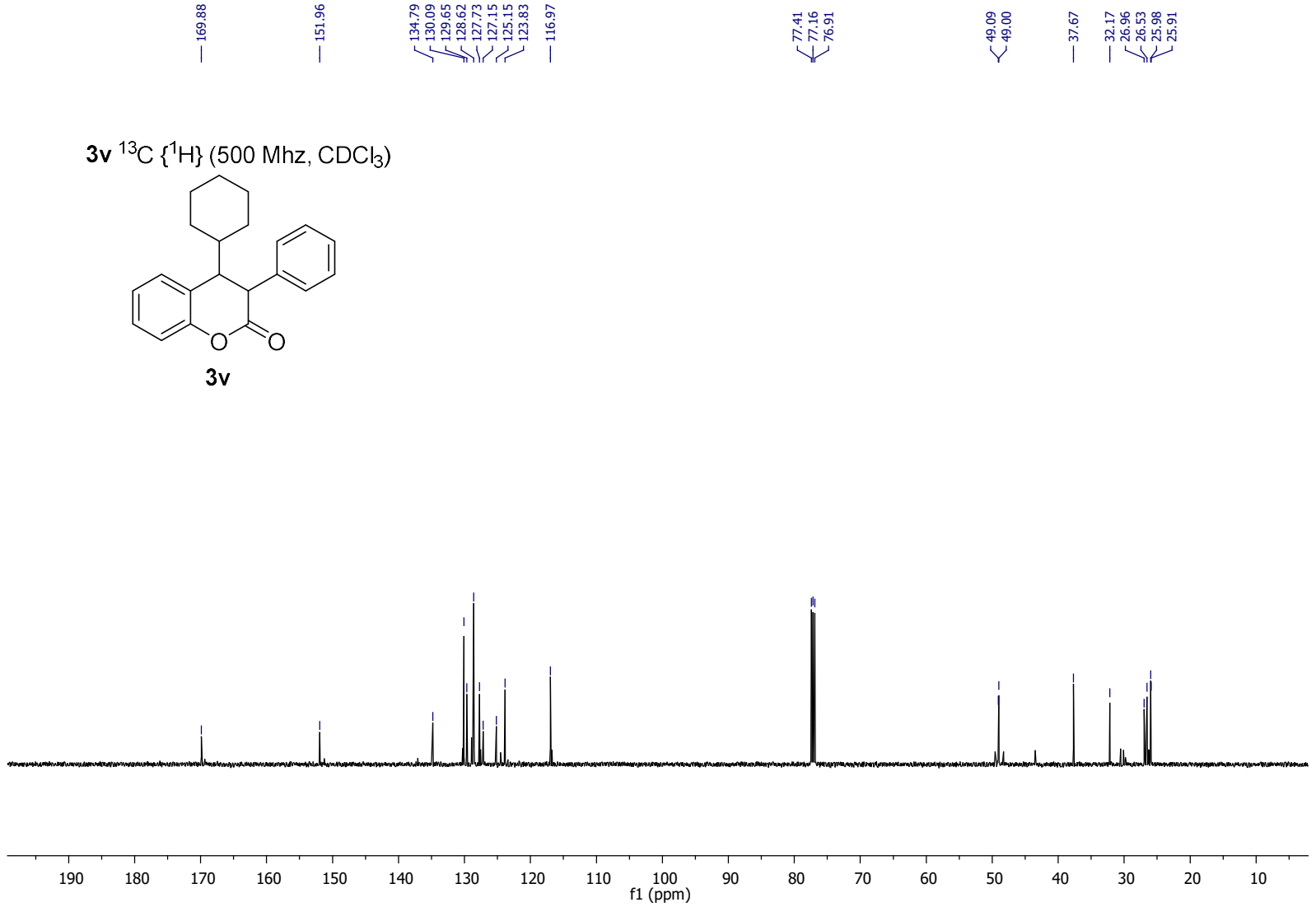

166.91
165.70
151.47
130.07
128.73
124.23
123.80
116.93
83.49
77.41
77.16
76.91
50.95
46.79
40.97
30.80
30.17
27.53
26.17
26.12
3u ^{13}C {^{1}H} (126 Mhz, $CDCl_3$)
O
O
O
O
3u
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

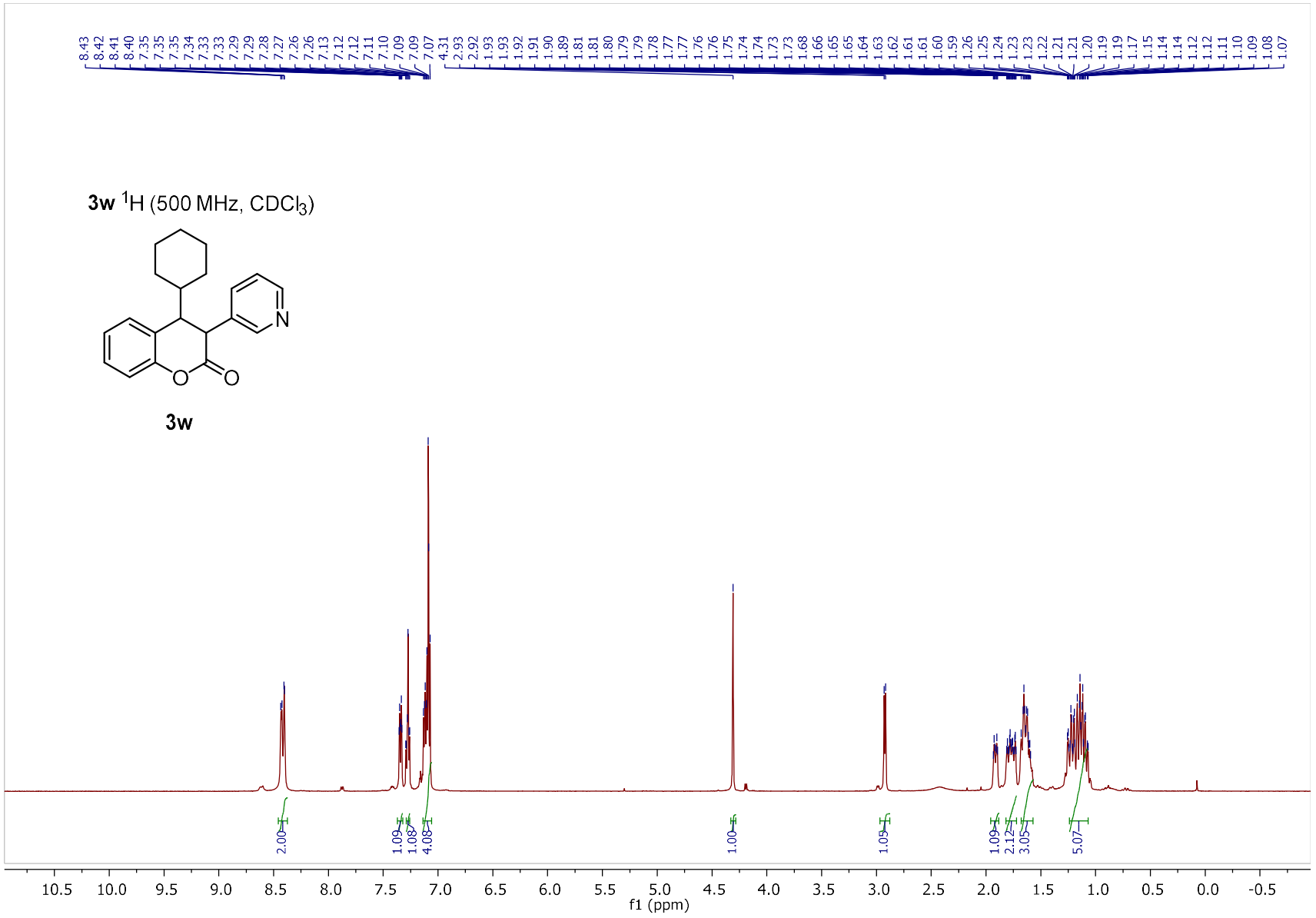
3v ^{1}H (500 Mhz, $CDCl_3$)

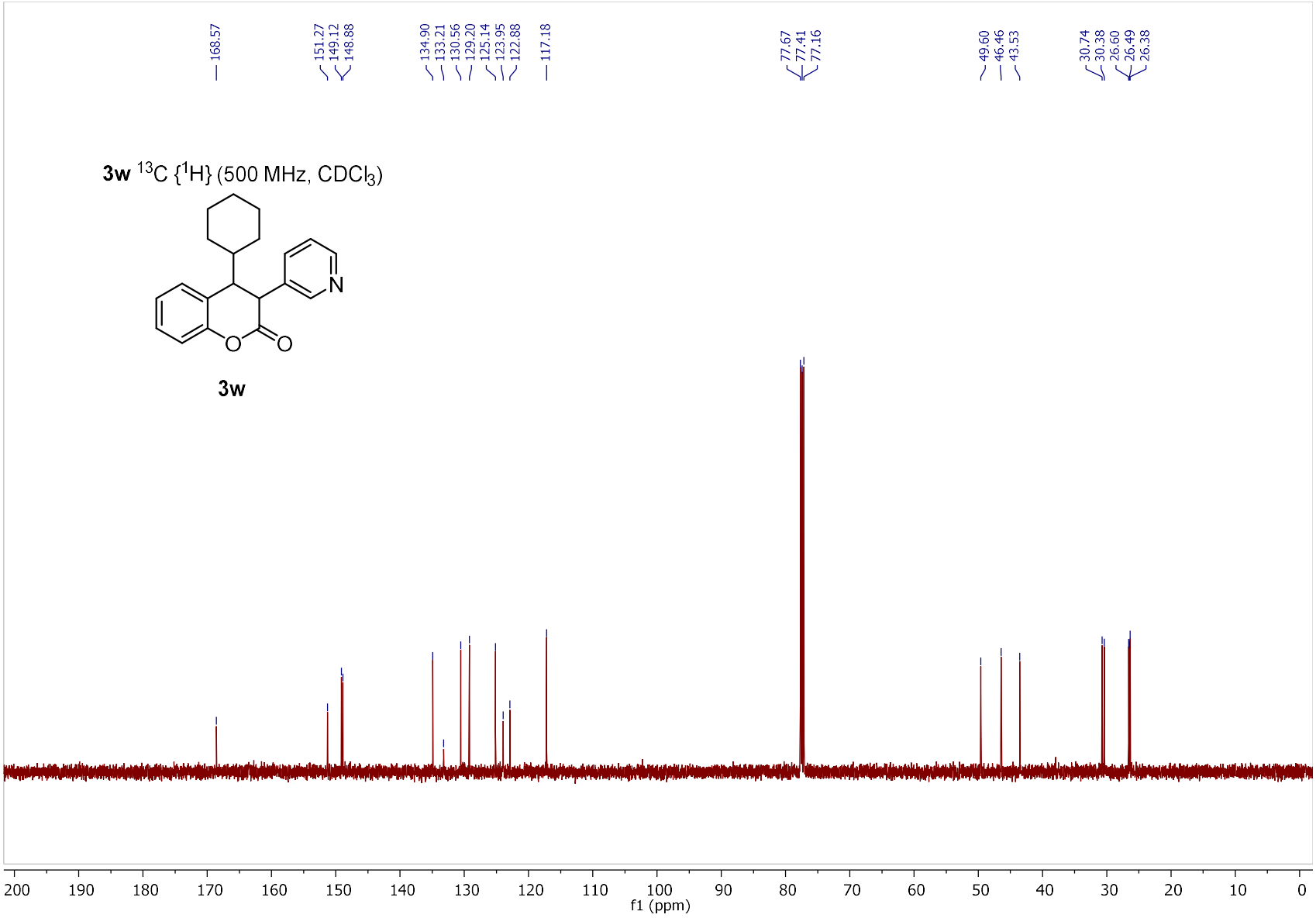


3v

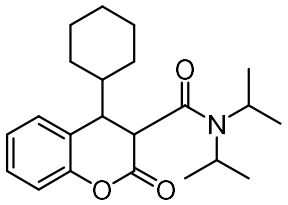



169.88
151.96
134.79
130.09
129.65
128.62
127.73
127.15
125.15
123.83
116.97
77.41
77.16
76.91
49.09
49.00
37.67
32.17
26.96
26.53
25.98
25.91
3v ^{13}C {^{1}H} (500 Mhz, $CDCl_3$)
O
O
3v
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

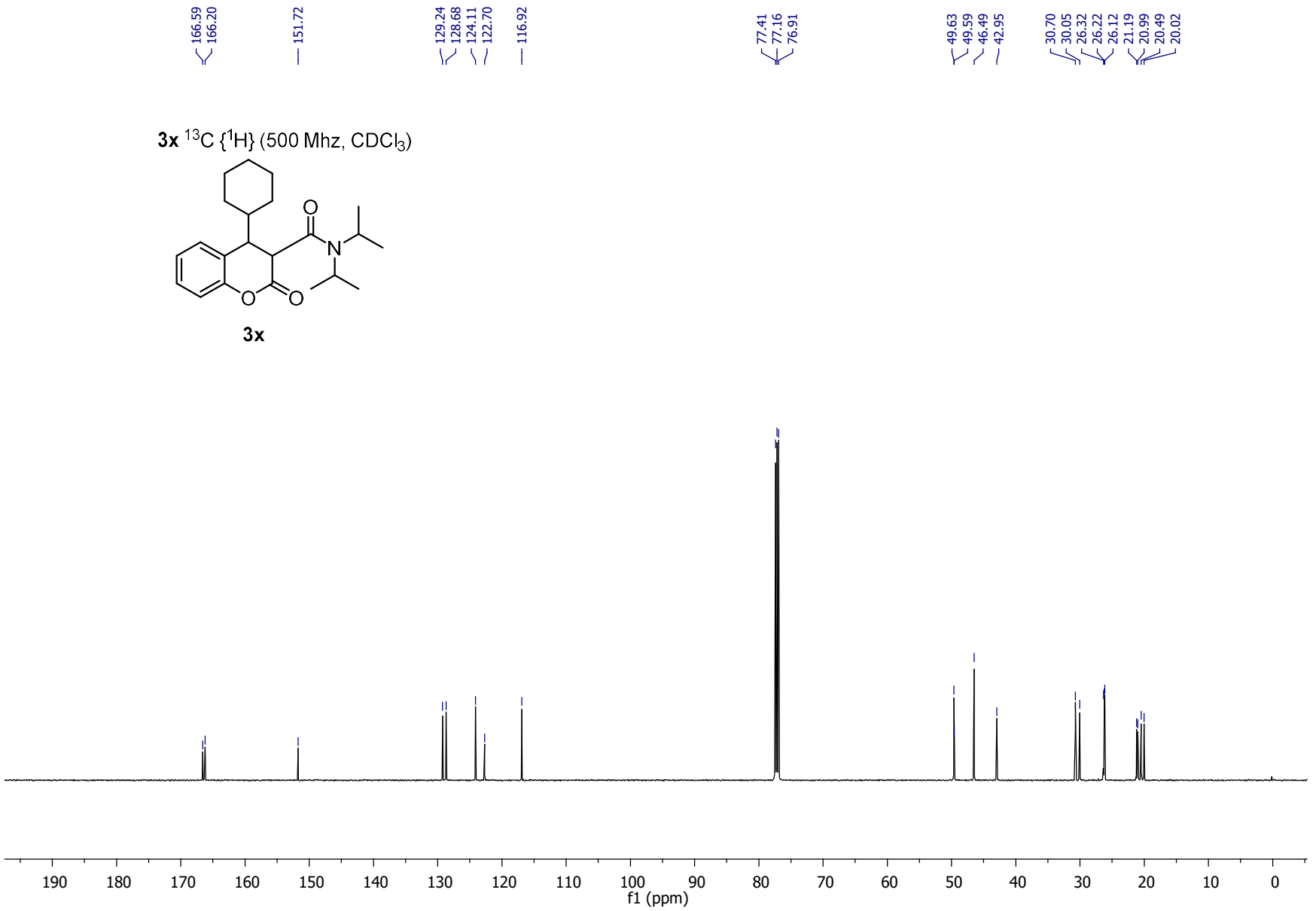

8.43 8.42 8.41 8.40 7.35 7.35 7.35 7.34 7.33 7.33 7.29 7.29 7.28 7.27 7.26 7.26 7.13 7.12 7.12 7.11 7.10 7.09 7.09 7.07 4.31 2.93 2.92 1.93 1.93 1.92 1.91 1.90 1.89 1.81 1.81 1.80 1.79 1.79 1.78 1.77 1.77 1.76 1.76 1.75 1.74 1.74 1.73 1.73 1.68 1.66 1.65 1.65 1.64 1.63 1.62 1.61 1.61 1.60 1.59 1.26 1.25 1.24 1.23 1.23 1.22 1.21 1.21 1.20 1.19 1.19 1.17 1.15 1.14 1.14 1.12 1.12 1.11 1.10 1.09 1.08 1.07
3w ^{1}H (500 MHz, $CDCl_3$)
N
O
O
3w
2.00
1.09
1.08
4.08
1.00
1.09
1.09
2.12
3.05
5.07
10.5 10.0 9.5 9.0 8.5 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 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

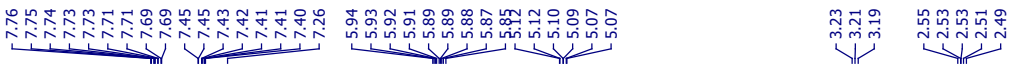

168.57
151.27
149.12
148.88
134.90
133.21
130.56
129.20
125.14
123.95
122.88
117.18
77.67
77.41
77.16
49.60
46.46
43.53
30.74
30.38
26.60
26.49
26.38
3w ^{13}C {^{1}H} (500 MHz, $CDCl_3$)
N
O
O
3w
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3x ^{1}H (500 Mhz, $CDCl_3$)

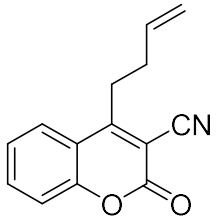


3x

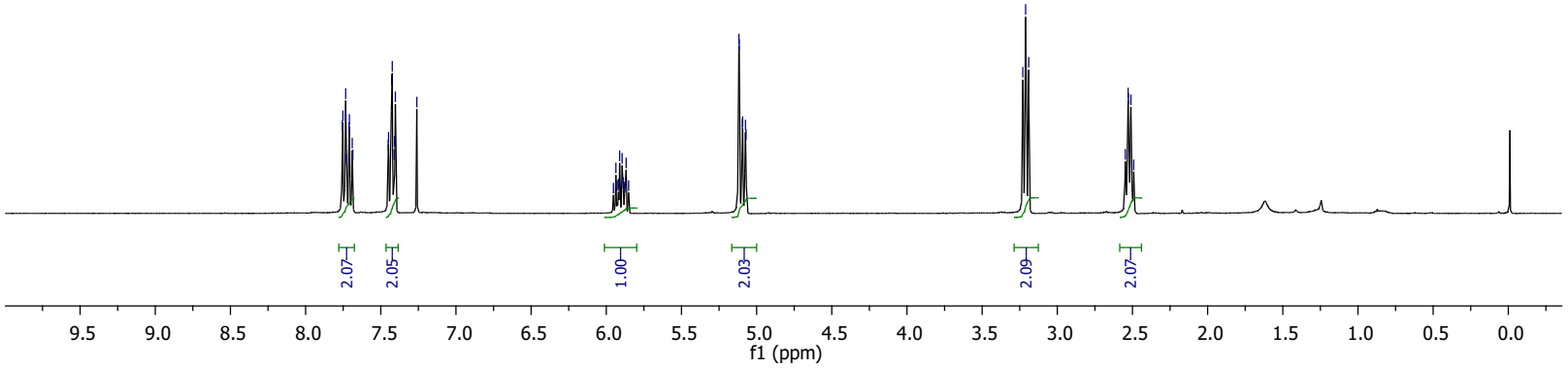

166.59
166.20
151.72
129.24
128.68
124.11
122.70
116.92
77.41
77.16
76.91
49.63
49.59
46.49
42.95
30.70
30.05
26.32
26.22
26.12
21.19
20.99
20.49
20.02
3x ^{13}C {^{1}H} (500 Mhz, $CDCl_3$)
O
N
O
O
3x
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

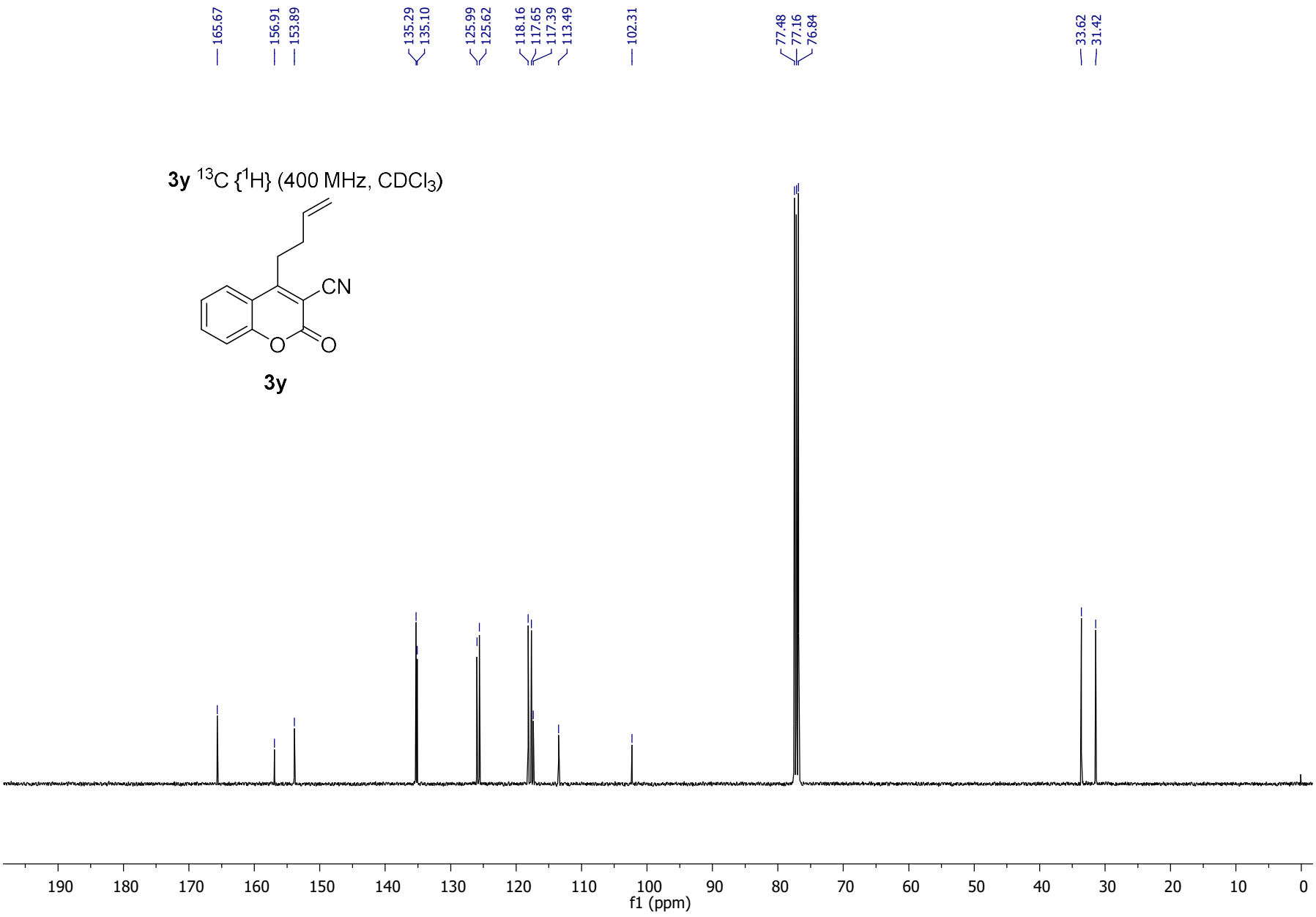


3y ^{1}H (400 MHz, $CDCl_3$)



3y




165.67
156.91
153.89
135.29
135.10
125.99
125.62
118.16
117.65
117.39
113.49
102.31
77.48
77.16
76.84
33.62
31.42
3y ^{13}C {^{1}H} (400 MHz, $CDCl_3$)
CN
O
O
3y
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)