Diazo Compounds as Highly Tunable Reactants in 1,3-Dipolar Cycloaddition Reactions with Cycloalkynes

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Table of Contents

1. Gaussian Calculations

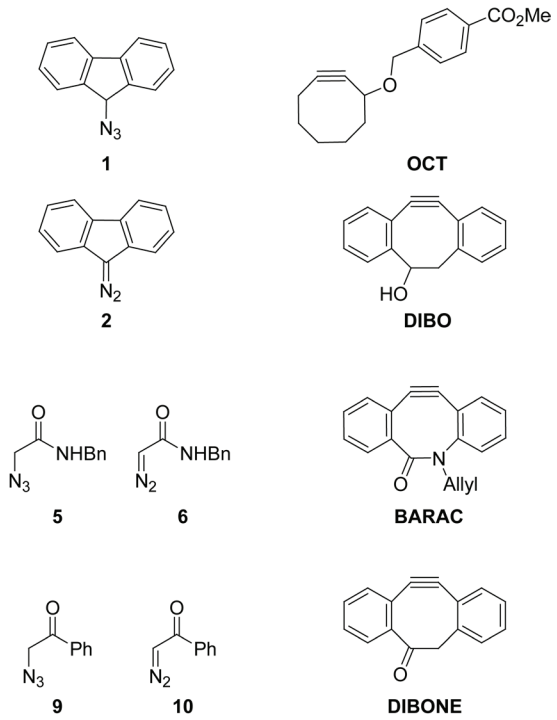
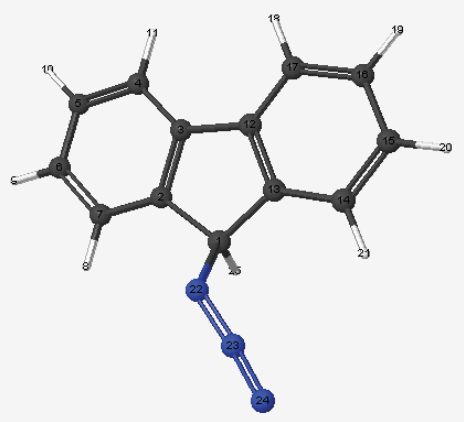


Table S1. Calculated Orbital Energies (MP2/cc-PVTZ) (kcal/mol)[1]

Dipole	HOMO	LUMO
1	–185.235	52.033
2	–172.754	46.303
5	–209.199	72.791
6	–208.986	60.831
9	–220.043	41.660
10	–217.828	44.785

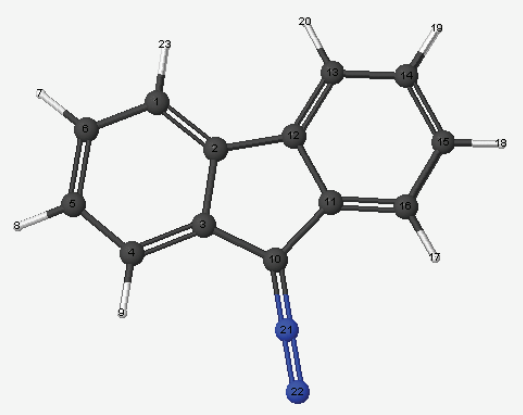
Alkyne	HOMO	LUMO
OCT	–212.312	50.966
DIBO	–180.792	41.792
BARAC	–181.231	38.222
DIBONE	–187.205	36.728

Azidofluorene **1**



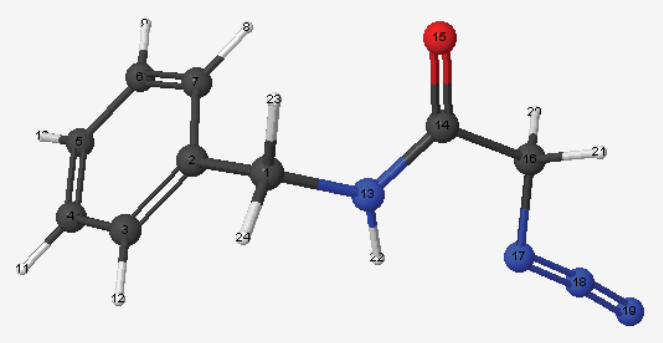
```
-----------------
 #N MP2/cc-pVTZ SP
-----------------
Alpha occ. eigenvalues -- -0.38222 -0.34312 -0.34150 -0.29519
Alpha virt. eigenvalues -- 0.08292 0.09459 0.13492 0.13807 0.14313
```

Diazofluorene **2**



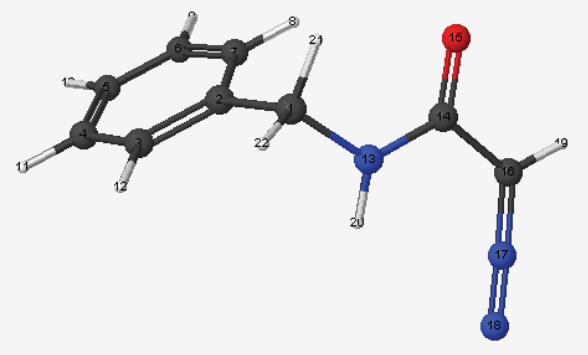
```
-----------------
 #N MP2/cc-pVTZ SP
-----------------
Alpha occ. eigenvalues -- -0.41872 -0.38165 -0.34508 -0.29120 -0.27530
Alpha virt. eigenvalues -- 0.07379 0.09007 0.11230 0.13468 0.14473
```

Azido-*N*-Benzylacetamide **5**



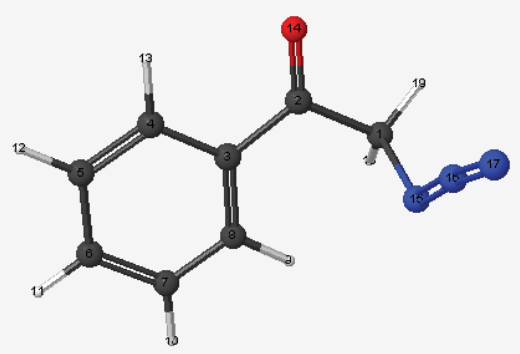
```
-----------------
 #N MP2/cc-pVTZ SP
-----------------
Alpha occ. eigenvalues -- -0.43325 -0.40487 -0.38946 -0.34009 -0.33338
Alpha virt. eigenvalues -- 0.11600 0.12124 0.12604 0.14058 0.14703
```

Diazo-*N*-Benzylacetamide **6**



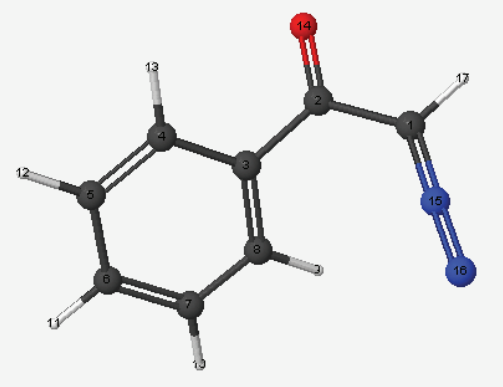
```
-----------------
 #N MP2/cc-pVTZ SP
-----------------
Alpha occ. eigenvalues -- -0.33304
Alpha virt. eigenvalues -- 0.09694 0.11011 0.12068 0.12673 0.13920
```

Azidoacetophenone **9**



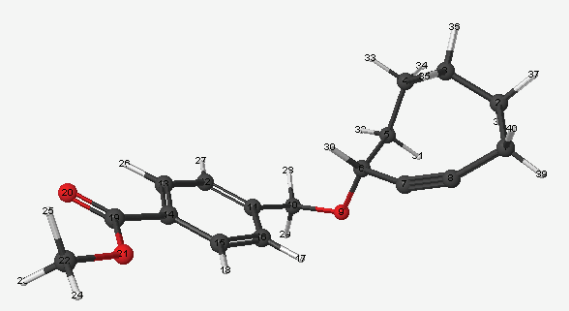
```
-----------------
 #N MP2/cc-pVTZ SP
-----------------
Alpha occ. eigenvalues -- -0.35284 -0.35066
Alpha virt. eigenvalues -- 0.06639 0.11512 0.12325 0.14347 0.15838
```

Diazoacetophenone **10**



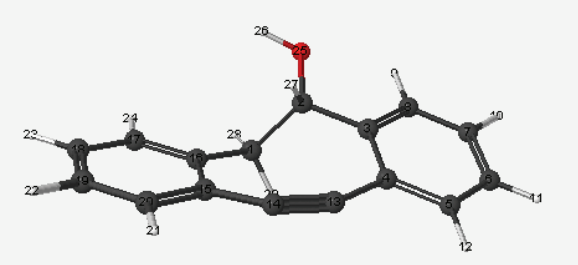
```
-----------------
 #N MP2/cc-pVTZ SP
-----------------
Alpha occ. eigenvalues -- -0.35520 -0.35007 -0.34713
Alpha virt. eigenvalues -- 0.07137 0.10038 0.11545 0.12941 0.14184
```

OCT



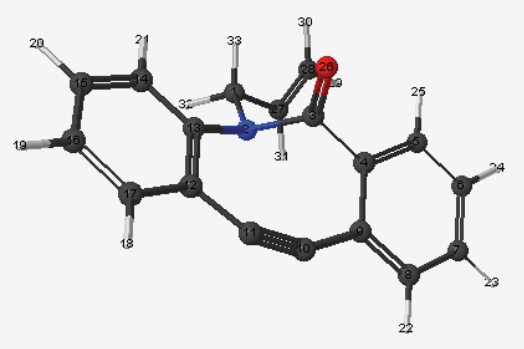
```
------------------------------
 #N MP2(FullDirect)/cc-pVTZ SP
------------------------------
Alpha occ. eigenvalues -- -0.35500 -0.34375 -0.33834
Alpha virt. eigenvalues -- 0.08122 0.11386 0.12975 0.13715 0.14374
```

DIBO



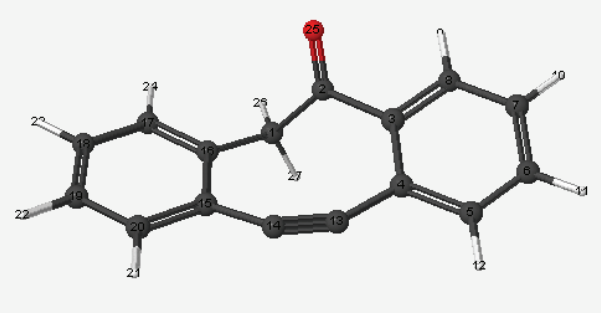
```
-----------------
 #N MP2/cc-pVTZ SP
-----------------

Alpha occ. eigenvalues -- -0.34023 -0.33051 -0.28811
Alpha virt. eigenvalues -- 0.06660 0.11118 0.11744 0.12364 0.13601
```

BARAC



```
-----------------
 #N MP2/cc-pVTZ SP
-----------------
Alpha occ. eigenvalues -- -0.34381 -0.32803 -0.28881
Alpha virt. eigenvalues -- 0.06091 0.08977 0.11031 0.11870 0.13237
```

DIBONE



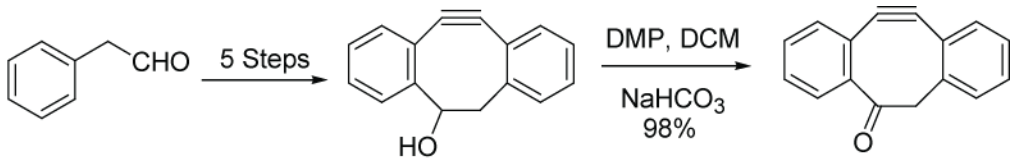
```
-----------------
 #N MP2/cc-pVTZ SP
 -----------------
Alpha occ. eigenvalues -- -0.34257 -0.29833
Alpha virt. eigenvalues -- 0.05853 0.09057 0.11712 0.11927 0.13862
```

2. General Methods

Reagent chemicals were obtained from commercial sources and used without further purification. All glassware was flame-dried under vacuum, and reactions were performed under N_2(g) unless indicated otherwise. Dichloromethane, diethyl ether, tetrahydrofuran, and toluene were dried over a column of alumina. Dimethylformamide and triethylamine were dried over alumina and purified further by passage through an isocyanate scrubbing column. Flash chromatography was performed with columns of 40–63 Å silica gel, 230–400 mesh (Silicycle, Québec City, Canada). Thin-layer chromatography (TLC) was performed on plates of EMD 250-μm silica 60-F_{254}. The phrase "concentrated under reduced pressure" refers to the removal of solvents and other volatile materials using a rotary evaporator at water aspirator pressure (<20 torr) while maintaining the water-bath temperature below 40 °C. Residual solvent was removed from samples at high vacuum (<0.1 torr). The term "high vacuum" refers to vacuum achieved by mechanical belt-drive oil pump. All NMR spectra were acquired at ambient temperature with a Bruker DMX-400 Avance, Bruker Avance III 500i with cryoprobe, or Bruker Avance III 500ii with cryoprobe spectrometer at the National Magnetic Resonance Facility at Madison (NMRFAM), and were referenced to TMS or a residual protic solvent. Electrospray ionization (ESI) mass spectrometry was performed with a Micromass LCT at the Mass Spectrometry Facility in the Department of Chemistry at the University of Wisconsin–Madison.

3. Experimental Procedures and Characterization Data

A. Synthesis of 4-Dibenzocyclooctynone (DIBONE)



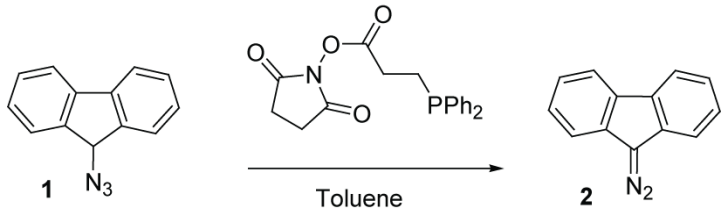
4-Dibenzocyclooctynol was prepared following literature procedures,[2-4] and resulted in identical spectral data and comparable yields in each synthetic transformation.

4-Dibenzocyclooctynone was prepared as described below. An analogous synthesis was reported recently[5] using similar procedures and yields.

4-Dibenzocyclooctynol (0.164 g, 0.745 mmol) was added to a flame-dried 25-mL round-bottom flask and dissolved in anhydrous DCM (7.5 mL) under an Ar(g) atmosphere. To this solution was added an equal-mass mixture of Dess–Martin Periodinane (0.348 g, 0.820 mmol), and sodium bicarbonate (0.348 g, 4.14 mmol) portion-wise over 10 min. After the addition was complete, the reaction mixture was allowed to stir for an additional 10 min, at which point TLC analysis (30% EtOAc, 70% hexanes) indicated complete conversion. The reaction mixture was diluted with distilled water and extracted with DCM. The combined extracts were dried over anhydrous sodium sulfate, combined, concentrated under reduced pressure, and purified by silica gel chromatography (30% EtOAc, 70% hexanes) to give 4-dibenzocyclooctynone as an amorphous white solid (0.160 g, 98%). All spectral data matched those reported previously.

4-Dibenzocyclooctynone: **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.58 (d, J = 7.6, 1H), 7.54–7.51 (m, 2H), 7.44–7.34 (m, 5H), 4.21 (d, J = 12.2, 1H), 3.68 (d, J = 12.2, 1H). **^{1}H NMR** (400 MHz, CD_3CN) δ 7.59–7.33 (m, 8H), 4.13 (d, J = 12.6, 1H), 3.68 (d, J = 12.6, 1H).

B. Synthesis of Azides and Diazo Compounds



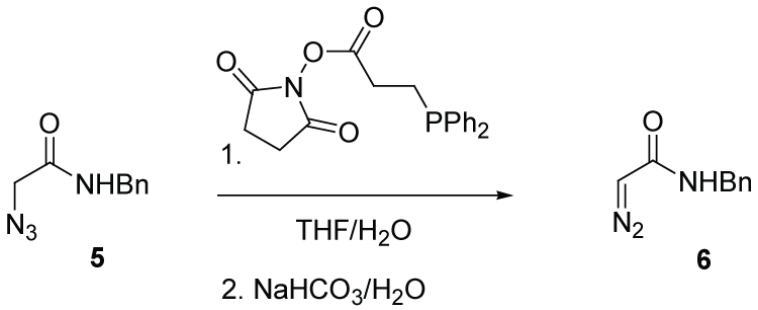
Azidofluorene (**1**) was prepared as reported previously[6] from the corresponding bromofluorene by treatment with sodium azide in aqueous acetone. The spectral data and yields matched those reported previously.

Azidofluorene (1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, J = 7.4, 2H), 7.63 (d, J = 7.4, 2H), 7.45 (t, J = 7.4, 2H), 7.37 (t, J = 7.4, 2H), 5.21 (s, 1H). **^{1}H NMR** (500 MHz, CD_3CN) δ 7.84 (d, J = 7.5, 2H), 7.70 (d, J = 7.4, 2H), 7.52 (t, J = 7.4, 2H), 7.44 (t, J = 7.5, 2H), 5.43 (s, 1H).

The synthesis of 9-diazo-fluorene was modified slightly from the initial report[3] and was achieved as follows.

Azidofluorene **1** (1.000 g, 4.831 mmol) was dissolved in anhydrous toluene (40 mL) at 0 °C under Ar(g) in a flame-dried 100-mL round-bottom flask. To this solution was added phosphine–NHS-ester (1.802 g, 5.073 mmol) portion-wise over 30 min. The reaction mixture was allowed to stir for 1 h at 0 °C before the bath was removed and the reaction mixture was warmed to room temperature while stirring over 8 h. The reaction was complete at this point by TLC analysis (10% EtOAc, 90% hexanes). The reaction mixture was concentrated to a total volume of ~2 mL, which was loaded directly on a plug of basic alumina and eluted with 10% EtOAc, 90% hexanes solution to give analytically pure diazofluorene **2** as a red amorphous solid (0.850 g, 92%). All spectral data matched those reported previously.

Diazofluorene (2): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, J = 7.5, 2H), 7.52 (d, J = 7.5, 2H), 7.39 (t, J = 7.5, 2H), 7.33 (t, J = 7.5, 2H). **^{1}H NMR** (400 MHz, CD_3CN) δ 8.06 (d, J = 7.6, 2H), 7.66 (d, J = 7.6, 2H), 7.45 (t, J = 7.4, 2H), 7.38 (t, J = 7.5, 2H).



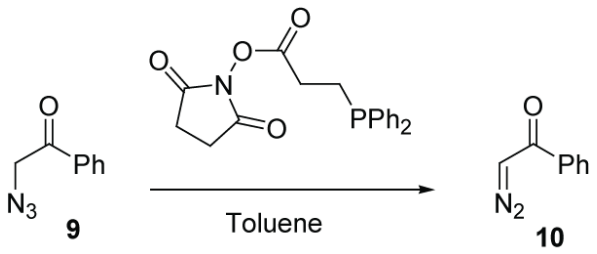
Azidobenzylacetamide (**5**) was prepared as reported previously[3] from the corresponding bromobenzylacetamide by treatment with sodium azide in aqueous THF. The spectral data and yields matched those reported previously.

Azidobenzylacetamide (5): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42–7.22 (m, 5H), 6.60 (s, 1H), 4.48 (d, J = 5.8, 2H), 4.05 (s, 2H). **^{1}H NMR** (500 MHz, CD_3CN) δ 7.42–7.25 (m, 5H), 7.16 (s, 1H), 4.42 (d, J = 6.0, 2H), 3.90 (s, 2H).

The synthesis of diazo-benzylacetamide (**6**) was modified slightly from the initial report[3] and was achieved as follows.

Azidobenzylacetamide **5** (0.500 g, 2.630 mmol) was dissolved in 10% H_2O/90% THF (20 mL) at room temperature in a 100-mL round-bottom flask. To this solution was added phosphine–NHS-ester (0.981 g, 2.762 mmol), and the reaction mixture was allowed to stir for 4 h at room temperature before a saturated solution of bicarbonate (17.5 mL) was added. The reaction mixture was stirred vigorously for 3 h. The reaction mixture was then diluted with brine and extracted with dichloromethane. The organics were dried over anhydrous sodium sulfate, concentrated under reduced pressure, and purified with silica gel chromatography (50% EtOAc/hexanes) to give pure diazobenzylacetamide **6** as a white solid (0.428 g, 93%). All spectral data matched those reported previously.

Diazobenzylacetamide (6): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37–7.27 (m, 5H), 5.25 (s, 1H), 4.72 (s, 1H), 4.49 (s, 2H). **^{1}H NMR** (500 MHz, CD_3CN) δ 7.44–7.24 (m, 5H), 6.48 (s, 1H), 5.04 (s, 1H), 4.41 (d, J = 5.5, 2H).



Azidoacetophenone (**9**) was prepared as reported previously[3] from the corresponding bromoacetophenone by treatment with sodium azide in aqueous acetone. The spectral data and yields matched those reported previously.

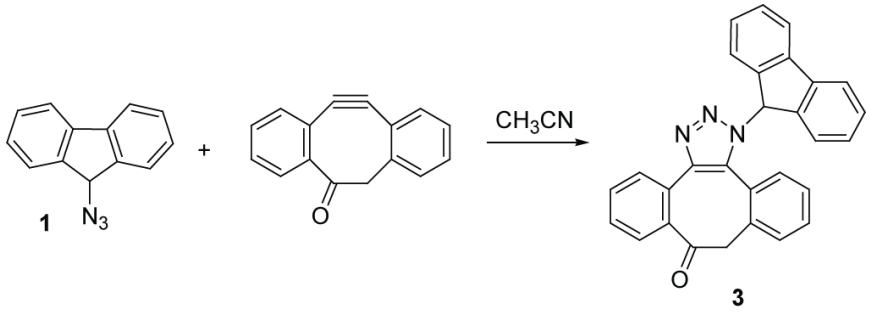
Azidoacetophenone (9): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, J = 7.8, 2H), 7.63 (t, J = 7.2, 1H), 7.51 (at, J = 7.5, 2H), 4.57 (s, 2H). **^{1}H NMR** (500 MHz, CD_3CN) δ 7.97 (d, J = 7.7, 2H), 7.70 (t, J = 7.1, 1H), 7.57 (t, J = 7.7, 2H), 4.71 (s, 2H).

The synthesis of diazoacetophenone (**10**) was modified slightly from the initial report[3] and was achieved as follows.

Azidoacetophenone **9** (0.533 g, 3.311 mmol) was dissolved in anhydrous toluene (16.55 mL) at 0 °C under Ar(g). To this solution was added phosphine–NHS-ester (1.235 g, 3.477 mmol), and the reaction mixture was allowed to stir for 2 h at 0 °C, and then warmed to room temperature over 2 h. The reaction mixture was then diluted with dichloromethane (20 mL) and stirred for 30 min before concentrating under vacuum. The resulting solid was purified by silica gel chromatography (20% EtOAc/hexanes) to give pure diazoacetophenone **10** as a yellow solid (0.460 g, 95%). All spectral data matched those reported previously.

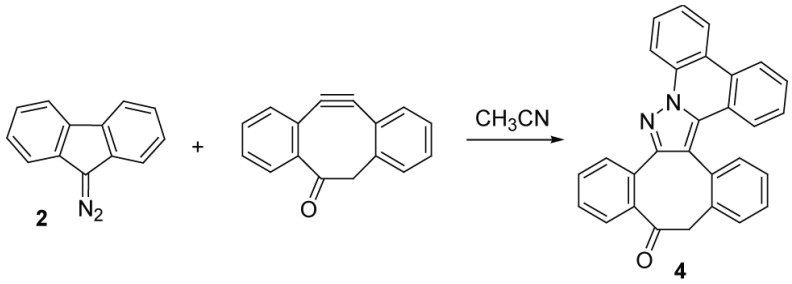
Diazoacetophenone (10): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, J = 7.7, 2H), 7.55 (t, J = 7.4, 1H), 7.45 (at, J = 7.4, 2H), 5.90 (s, 1H). **^{1}H NMR** (500 MHz, CD_3CN) δ 7.83 (d, J = 7.5, 2H), 7.63 (t, J = 7.2, 1H), 7.53 (t, J = 7.5, 2H), 6.28 (s, 1H).

C. [3+2] Cycloaddition Reactions



Azidofluorene **1** (0.007 g, 0.034 mmol) was dissolved in anhydrous acetonitrile (0.68 mL) in a scintillation vial at room temperature under stirring. To this solution was added a solution of **DIBONE** (0.007 g, 0.034 mmol) in anhydrous acetonitrile (0.68 mL) and the reaction progress was monitored by thin-layer chromatography (30% EtOAc, 70% hexanes). After the reaction was judged to be complete (35 min), the reaction mixture was concentrated under reduced pressure and purified by silica gel chromatography to give a mixture of triazoles **3** (0.013 g, 93%).

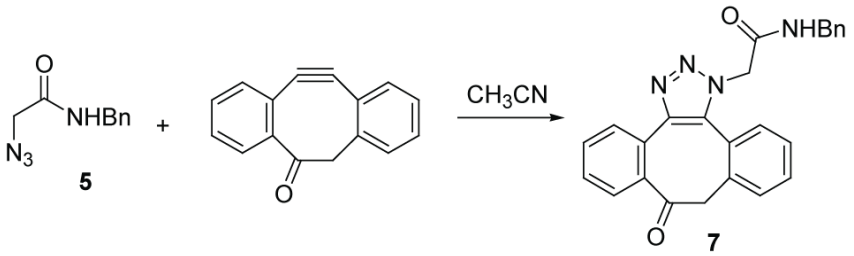
Fluorenyl Triazoles: **^{1}H NMR (400 MHz, $CDCl_3$)** (Mixture of Triazoles) δ 8.21 (d, J = 7.9, 1H), 7.93 (d, J = 7.8, 1H), 7.75–7.55 (m, 4H), 7.54–7.47 (m, 2H), 7.45–7.35 (m, 3H), 7.33–7.27 (m, 1H), 7.20–7.05 (m, 4H), 7.00–6.91 (m, 1H), 3.92 (d, J = 14.8, 0.30H), 3.79–3.58 (m, 1.70H); **^{13}C NMR (126 MHz, $CDCl_3$)** (Mixture of Triazoles) δ 197.8, 195.8, 147.4, 146.0, 142.5, 142.3, 140.8, 140.6, 140.1, 139.9, 134.3, 133.5, 133.1, 132.8, 130.9, 130.8, 130.7, 130.4, 130.3, 129.9, 129.6, 129.6, 129.5, 129.4, 129.1, 128.7, 128.3, 128.2, 128.2, 127.8, 127.7, 127.0, 126.6, 125.6, 125.0, 124.8, 124.2, 124.0, 120.8, 120.7, 120.3, 120.3, 64.8, 64.8, 50.0, 48.5; **HRMS** (ESI) m/z 426.1599 [calc'd for $C_{29}H_{20}N_3O$ (M+H) 426.1601].



Diazofluorene **2** (0.009 g, 0.046 mmol) was dissolved in anhydrous acetonitrile (0.92 mL) in a scintillation vial at room temperature under stirring. To this solution was added a solution of **DIBONE** (0.010 g, 0.046 mmol) in anhydrous acetonitrile (0.92 mL) and the reaction progress was monitored by thin-layer chromatography (30% EtOAc, 70% hexanes). After the reaction was judged to be complete (<5 min), the reaction mixture was concentrated under reduced pressure and purified by silica gel chromatography to give a mixture of pyrazoles **4** (0.017 g, 89%).

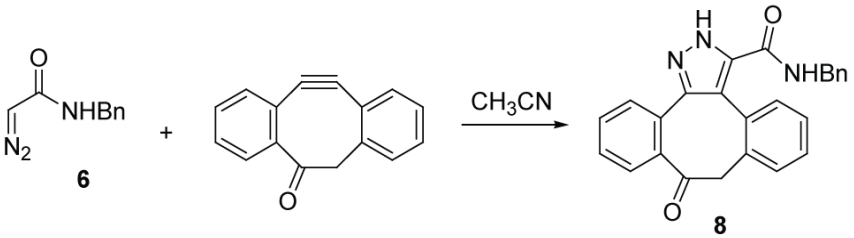
Fluorene-Derived Pyrazoles: **^{1}H NMR (400 MHz, $CDCl_3$)** (Mixture of Pyrazoles) δ 8.47 (d, J = 8.0, 1H), 8.42 (d, J = 7.9, 1H), 7.96 (d, J = 7.6, 1H), 7.87–7.74 (m, 2H), 7.71–7.51 (m, 2H), 7.49–7.33 (m, 4H), 7.24–7.13 (m, 2H), 7.09 (d, J = 7.3, 1H), 6.80 (t, J = 7.6, 1H), 6.42 (d, J = 7.9, 1H), 4.07–3.94 (m, 2H); **^{13}C NMR (126 MHz, $CDCl_3$)** (Mixture of Pyrazoles, Not all Olefinic Carbons Resolve) δ 199.3, 194.8, 155.1, 145.8, 145.0, 140.7, 138.8, 135.7, 133.6, 133.4, 132.5, 132.1, 132.0, 131.5, 131.1, 130.6, 130.6, 130.4, 129.9, 129.7, 129.3, 129.0, 128.8, 128.7, 128.0,

127.8, 127.4, 127.2, 126.9, 126.2, 124.9, 123.7, 121.4, 120.3, 118.8, 117.2, 111.5, 48.6, 48.1; **HRMS** (ESI) *m*/*z* 411.1505 [calc'd for $C_{29}H_{19}N_2O$ (M+H) 411.1492].



Azido-*N*-benzylacetamide **5** (0.006 g, 0.034 mmol) was dissolved in anhydrous acetonitrile (0.68 mL) in a scintillation vial at room temperature under stirring. To this solution was added a solution of **DIBONE** (0.007 g, 0.034 mmol) in anhydrous acetonitrile (0.68 mL) and the reaction progress was monitored by thin-layer chromatography (30% EtOAc, 70% hexanes). After the reaction was judged to be complete (40 min), the reaction mixture was concentrated under reduced pressure and purified by silica gel chromatography to give a mixture of triazoles **7** (0.012 g, 89%).

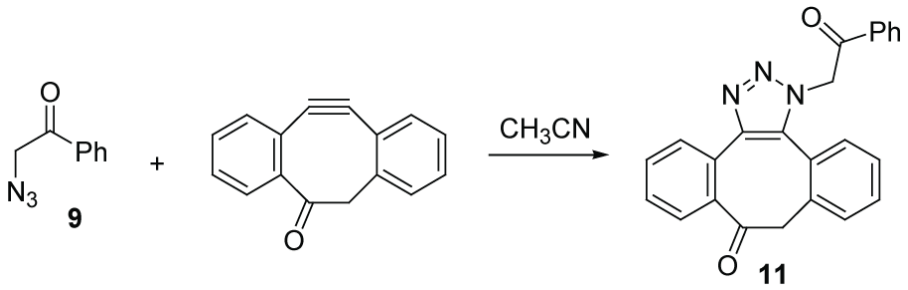
***N*-Benzylacetamide Triazoles: ^{1}H NMR (400 MHz, $CDCl_3$)** (Mixture of Triazoles) δ 8.32 (d, J = 8.3, 0.7H), 8.27 (d, J = 8.0, 0.3H), 7.98 (d, J = 7.7, 1H), 7.70–7.61 (m, 1H), 7.60–7.43 (m, 3H), 7.42–7.28 (m, 5H), 7.25–7.17 (m, 2H), 6.50 (s, 0.3H), 6.34 (s, 0.7H), 5.21 (d, J = 16.4, 1H), 5.03 (d, J = 16.4, 1H), 4.53 (dd, J = 5.8, 14.9, 1H), 4.43 (dd, J = 5.8, 14.9, 1H), 3.89–3.78 (m, 2H); **^{13}C NMR (126 MHz, $CDCl_3$)** (Mixture of Triazoles, Not all Olefinic Carbons Resolve) δ 196.7, 195.1, 165.0, 164.9, 146.5, 145.6, 137.1, 136.4, 135.9, 135.2, 134.9, 134.1, 133.3, 133.1, 133.0, 131.9, 131.4, 131.1, 131.0, 130.9, 130.2, 130.1, 130.0, 129.9, 129.6, 128.9, 128.8, 128.6, 128.2, 128.0, 128.0, 127.9, 127.8, 127.8, 125.4, 124.5, 51.9, 51.4, 49.4, 48.0, 44.0, 43.9; **HRMS** (ESI) *m*/*z* 431.1498 [calc'd for $C_{25}H_{20}N_4O_2Na$ (M+Na) 431.1479].



Diazo-*N*-benzylacetamide **6** (0.008 g, 0.046 mmol) was dissolved in anhydrous acetonitrile (0.92 mL) in a scintillation vial at room temperature under stirring. To this solution was added a solution of **DIBONE** (0.010 g, 0.046 mmol) in anhydrous acetonitrile (0.92 mL) and the reaction progress was monitored by thin-layer chromatography (30% EtOAc, 70% hexanes). After the reaction was judged to be complete (25 min), the reaction mixture was concentrated under reduced pressure and purified by silica gel chromatography to give a regioisomeric mixture of pyrazoles **8** (0.017 g, 94%).

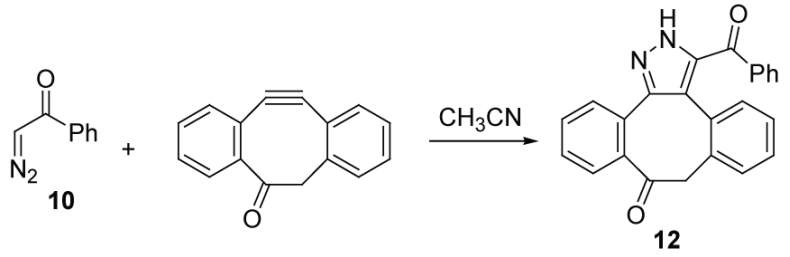
***N*-Benzylacetamide Pyrazoles: ^{1}H NMR (400 MHz, $CDCl_3$)** (Mixture of Pyrazoles) δ 8.20 (d, J = 7.9, 0.67H), 8.06 (d, J = 7.5, 0.33H), 7.57–7.16 (m, 13H), 6.82 (s, 1H), 4.72–4.62 (m, 1H), 4.49–4.37 (m, 1H), 4.05–3.84 (m, 2H); **^{13}C NMR (126 MHz, $CDCl_3$)** (Mixture of Pyrazoles, Not all Olefinic Carbons Resolve) δ 198.6, 197.5, 160.5, 160.1, 137.6, 137.5, 137.4, 136.1, 135.4, 134.4, 134.3, 133.8, 132.9, 132.0, 131.0, 130.8, 130.4, 130.2, 130.1, 129.7,

129.7, 129.2, 129.1, 128.8, 128.2, 128.0, 127.9, 127.8, 127.7, 127.4, 121.0, 119.8, 49.9, 49.4, 43.4,43.4; **HRMS** (ESI) *m*/*z* 416.1366 [calc'd for $C_{25}H_{19}N_3O_2Na$ (M+Na) 416.1370].



Azidoacetophenone **9** (0.005 g, 0.034 mmol) was dissolved in anhydrous acetonitrile (0.68 mL) in a scintillation vial at room temperature under stirring. To this solution was added a solution of **DIBONE** (0.007 g, 0.034 mmol) in anhydrous acetonitrile (0.68 mL) and the reaction progress was monitored by thin-layer chromatography (30% EtOAc, 70% hexanes). After the reaction was judged to be complete (60 min), the reaction mixture was concentrated under reduced pressure and purified by silica gel chromatography to give a regioisomeric mixture of triazoles **11** (0.011 g, 92%).

Acetophenone Triazoles: **^{1}H NMR (400 MHz, $CDCl_3$)** (Mixture of Triazoles) δ 8.31 (d, J = 8.0, 0.7H), 8.21 (d, J = 7.8, 0.3H), 8.02 (d, J = 7.8, 0.7H), 7.91–7.80 (m, 2H), 7.76–7.68 (m, 0.3H), 7.67–7.56 (m, 1.7H), 7.55–7.32 (m, 5.3H), 7.31–7.16 (m, 2H), 6.13 (d, J = 17.5, 0.3H), 5.91 (s, 1.4H), 5.81 (d, J = 17.5, 0.3H), 4.07–3.88 (m, 2H); **^{13}C NMR (101 MHz, $CDCl_3$)** (Mixture of Triazoles, Not all Olefinic Carbons Resolve) δ 197.1, 195.7, 190.4, 190.0, 146.3, 145.7, 136.4, 136.3, 135.5, 135.2, 134.6, 134.2, 133.8, 133.8, 133.7, 133.2, 133.1, 132.6, 131.8, 131.2, 131.0, 130.9, 130.4, 130.2, 130.1, 129.7, 129.6, 129.1, 128.7, 128.4, 128.0, 127.8, 127.7, 127.3, 126.3, 125.3, 54.9, 54.4, 49.3, 48.1; **HRMS** (ESI) *m*/*z* 380.1377 [calc'd for $C_{24}H_{18}N_3O_2$ (M+H) 380.1394].

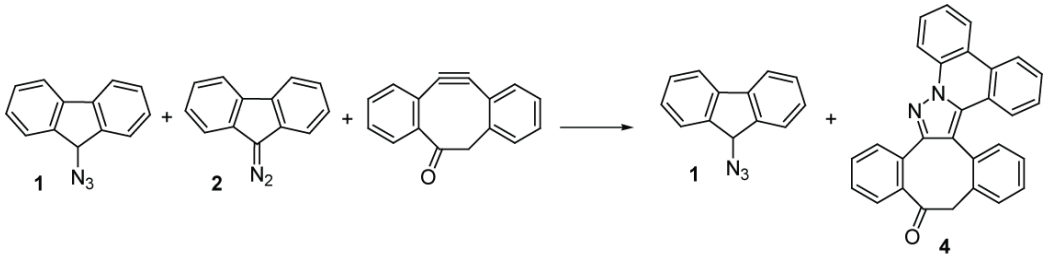


Diazoacetophenone **10** (0.007 g, 0.046 mmol) was dissolved in anhydrous acetonitrile (0.92 mL) in a scintillation vial at room temperature under stirring. To this solution was added a solution of **DIBONE** (0.010 g, 0.046 mmol) in anhydrous acetonitrile (0.92 mL) and the reaction progress was monitored by thin-layer chromatography (30% EtOAc, 70% hexanes). After the reaction was judged to be complete (1260 min), the reaction mixture was concentrated under reduced pressure and purified by silica gel chromatography to give a regioisomeric mixture of pyrazoles **12** (0.015 g, 88%).

Benzoyl Pyrazoles: **^{1}H NMR (400 MHz, $CDCl_3$)** (Mixture of Pyrazoles) δ 8.24 (d, J = 7.9, 0.7H), 8.06 (d, J = 8.3, 0.3H), 7.84–7.74 (m, 2H), 7.60–7.25 (m, 8H), 7.22–7.13 (m, 1H), 7.13–7.06 (m, 1H), 6.98 (t, J = 7.5, 0.7H), 6.87 (d, J = 7.8, 0.3H), 4.23–3.96 (m, 2H); **^{13}C NMR (101 MHz, $CDCl_3$)** (Mixture of Pyrazoles, Not all Olefinic Carbons

Resolve) δ 198.3, 197.5, 187.8, 187.7, 136.9, 136.7, 135.7, 135.6, 134.9, 135.5, 133.4, 133.2, 133.1, 132.3, 132.2, 131.6, 131.4, 131.0, 130.9, 130.9, 130.4, 130.1, 130.0, 129.5, 129.3, 128.9, 128.5, 128.3, 128.1, 127.9, 127.2, 124.2, 123.1, 50.0, 49.5; **HRMS** (ESI) *m/z* 387.1100 [calc'd for $C_{24}H_{16}N_2O_2Na$ (M+Na) 387.1104].

D. Kinetic Competition Experiments



Competitive kinetics were analyzed by dissolving 0.008 g (0.020 mmol each) of an equimolar mixture of azido and diazofluorene in dry acetonitrile (0.60 mL) at room temperature. To this solution was added a solution of **DIBONE** (0.0044 g, 0.020 mmol) in acetonitrile (0.20 mL), and the reaction mixture was allowed to run to completion. The reaction mixture was then concentrated and analyzed by ^{1}H-NMR spectroscopy ($CDCl_3$) which indicated the complete conversion of diazofluorene to the mixture of pyrazoles without any measurable conversion of azidofluorene to the corresponding triazoles (lack of 8.2 (t) as a representative signal).

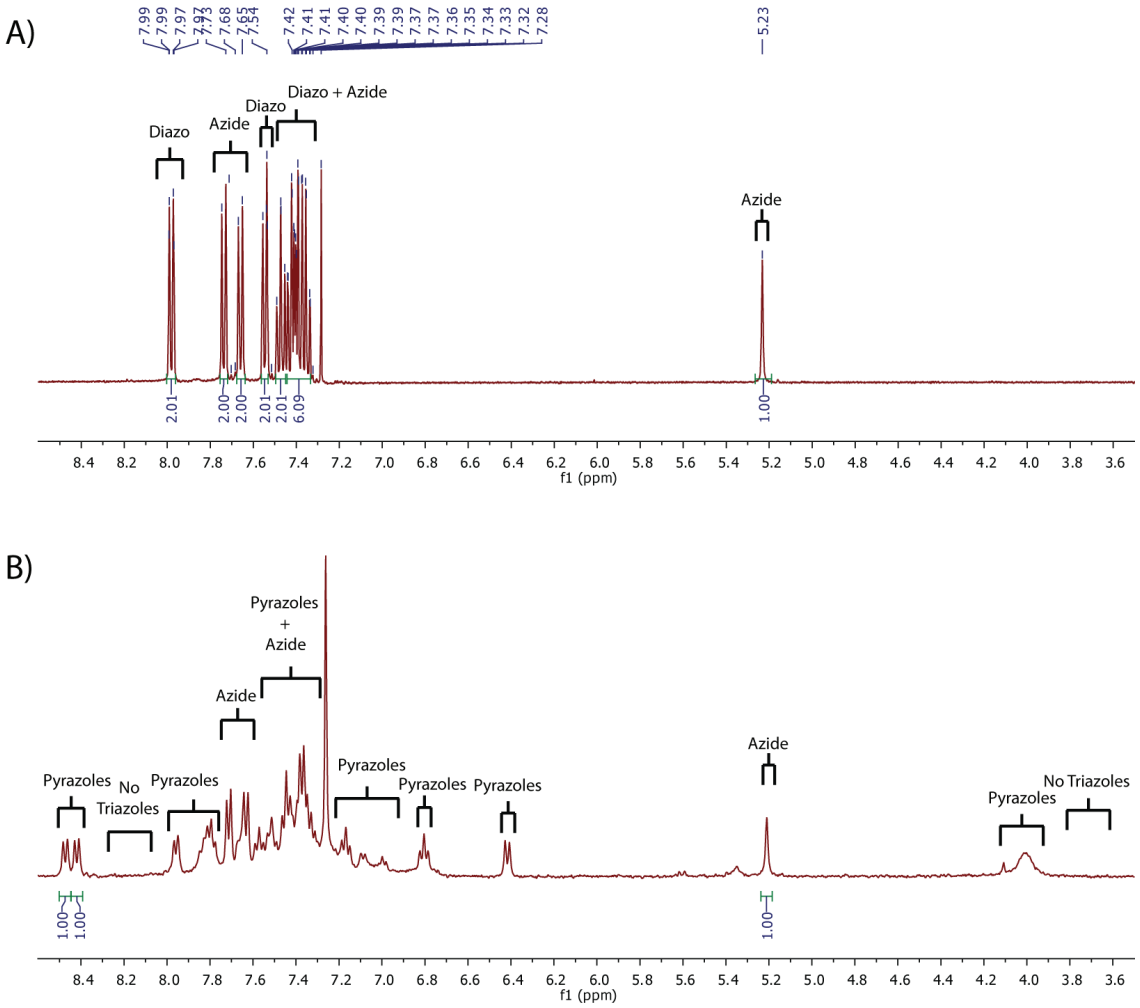
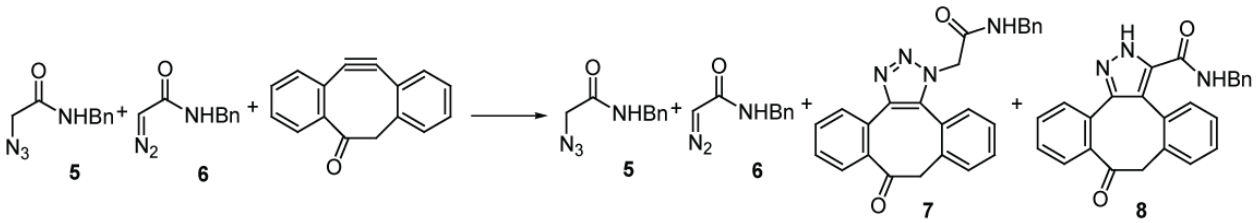


Fig. S1. Competition Kinetics (**1** *vs* **2**). A) Equimolar mixture of azide and diazo. B) Resulting NMR spectrum after adding 1 equiv of **DIBONE** relative to 1 equiv of azide and 1 equiv of diazo ($CDCl_3$).



Competitive kinetics were analyzed by taking 0.005 g (0.0137 mmol each) of an equimolar mixture of azido and diazo-*N*-benzylacetamide and dissolving it in dry acetonitrile (0.45 mL) at room temperature. To this solution was added a solution of **DIBONE** (0.0030 g, 0.0137 mmol) in acetonitrile (0.1 mL), and the reaction mixture was allowed to run to completion. The reaction mixture was then concentrated and analyzed by ^{1}H-NMR spectroscopy ($CDCl_3$) which indicated a 67% conversion of diazo-*N*-benzylacetamide to the mixture of pyrazoles (8.2 (d) and 8.1 (d)) and a 31% conversion of azido-*N*-benzylacetamide to the corresponding triazoles (8.35 (d) and 8.3 (d)).

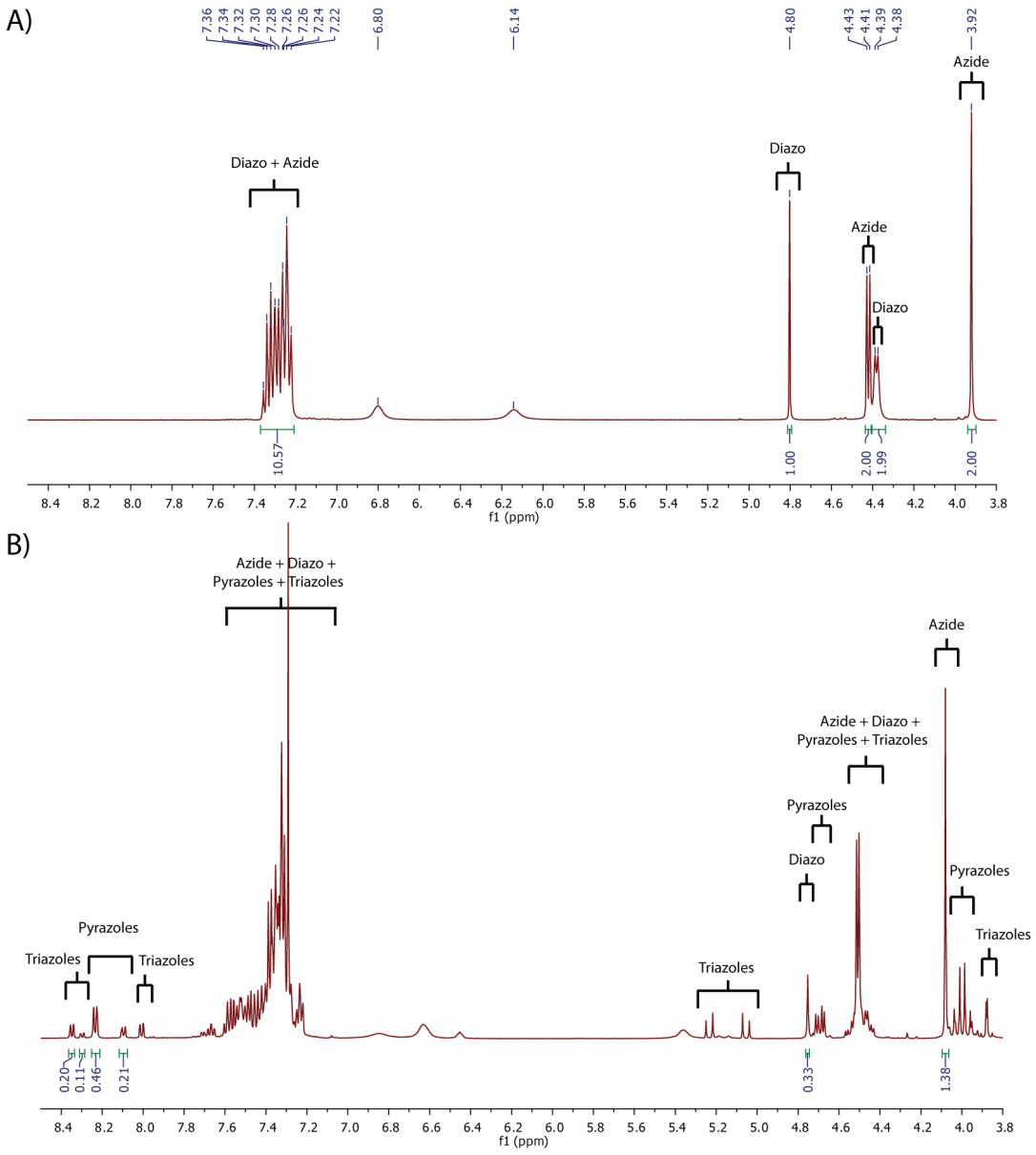
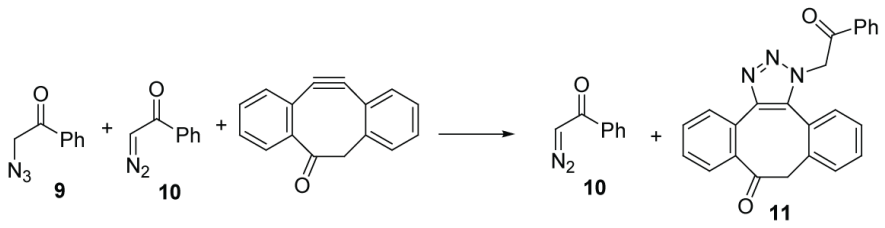


Fig. S2. Competition Kinetics (**5** *vs* **6**). A) Equimolar mixture of azide and diazo compound. B) Resulting NMR spectrum after adding 1 equiv of **DIBONE** relative to 1 equiv of azide and 1 equiv of diazo compound ($CDCl_3$).



Competitive kinetics were analyzed by taking 0.012 g (0.039 mmol each) of an equimolar mixture of azido and diazoacetophenone and dissolving it in dry acetonitrile (1.06 mL) at room temperature. To this solution was added a

solution of **DIBONE** (0.0085 g, 0.039 mmol) in acetonitrile (0.5 mL), and the reaction mixture was allowed to stir for 60 min. The reaction mixture was then concentrated and analyzed by ^{1}H-NMR spectroscopy ($CDCl_3$) which indicated the near complete conversion of azidoacetophenone to the mixture of triazoles without any measurable conversion of diazoacetophenone to the corresponding pyrazoles (lack of 7.0 (t) and 6.9 (d) as representative signals).

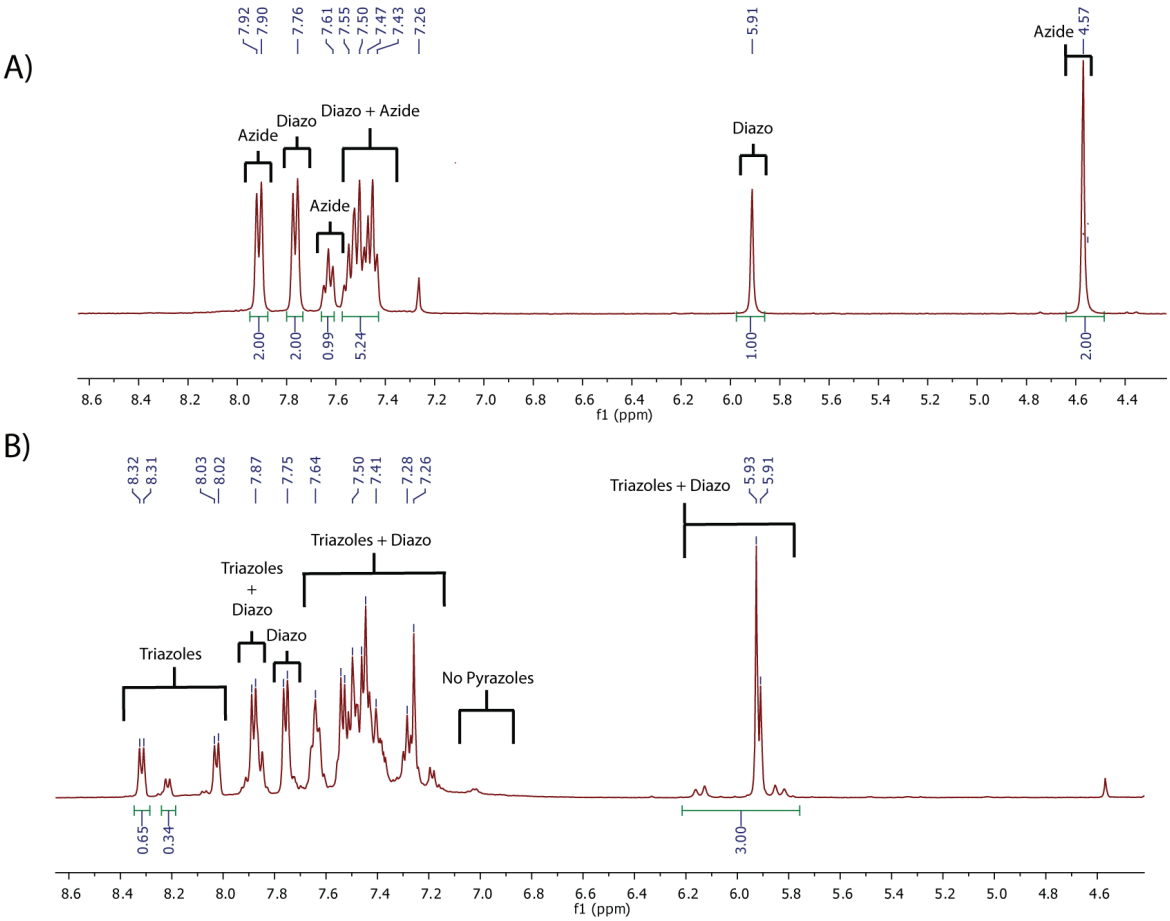


Fig. S3. Competition Kinetics (**9** *vs* **10**). A) Equimolar mixture of azide and diazo compound. B) Resulting NMR after adding 1 equiv of **DIBONE** relative to 1 equiv of azide and 1 equiv of diazo compound ($CDCl_3$).

4. NMR Kinetics Experiments

All NMR kinetics experiments were conducted in triplicate and the rate constants are reported as an average of the three values. The reactants were mixed in equal ratios at a concentration of 0.00319M in deuterated solvent. The components were combined, the NMR tube was inverted once and inserted into the spectrometer, and the scan was initialized exactly 20 s after initial mixing. A 16-scan NMR spectrum was acquired every 77 s, and the integrations were used to calculate concentrations from the known initial concentrations. The second-order rate constants were then determined from the slope of the plot of [**DIBONE**]$^{-1}$ *vs* time.

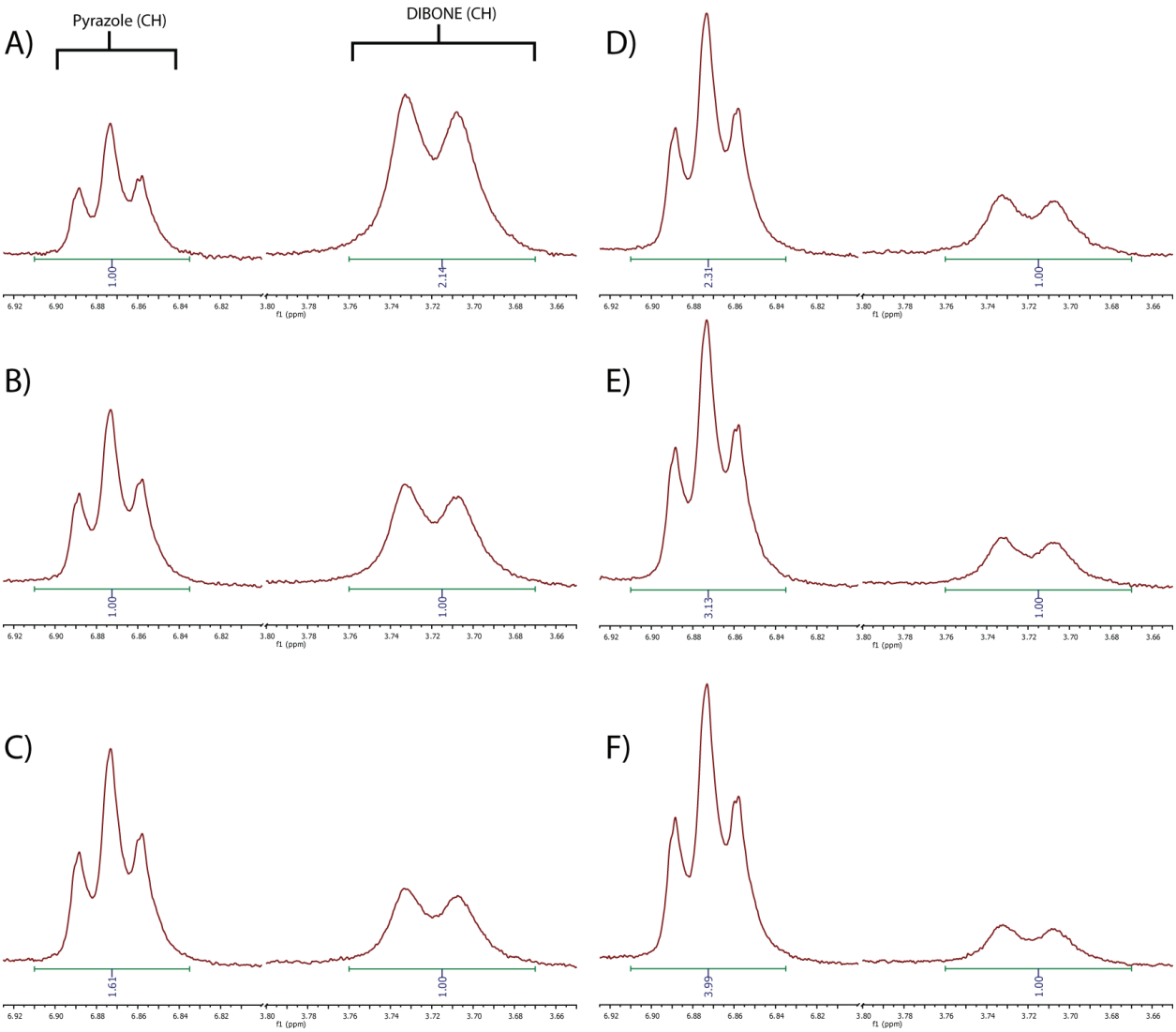


Fig. S4. Sample NMR kinetic analysis of **DIBONE** and diazofluorene **2** in CD_3CN. A) 58.5 s, B) 135.5 s, C) 212.5 s, D) 289.5 s, E) 366.5 s, F) 443.5 s.

We also reacted diazo compound **2** with **OCT** and **DIBO** in a similar manner. The kinetic rate constants confirm that **DIBONE** is the best partner for cycloaddition with diazo compound **2**.

Table S2. Calculated Energies and Second-Order Rate Constants for the Reaction of Diazo Compound **2** with Alkynes in CD_3CN

Alkyne	ΔE_{NED}[a] (kcal/mol)	k (M^{-1} s^{-1})
OCT	223.720	0.02
DIBO	214.546	0.13
DIBONE[b]	209.482	2.6

[a] $LUMO_{Alkyne} - HOMO_{\mathbf{2}}$ using data in Table S1.
[b] Data for **DIBONE** are also reported in the main text.

5. Demonstration of Chemoselectivity

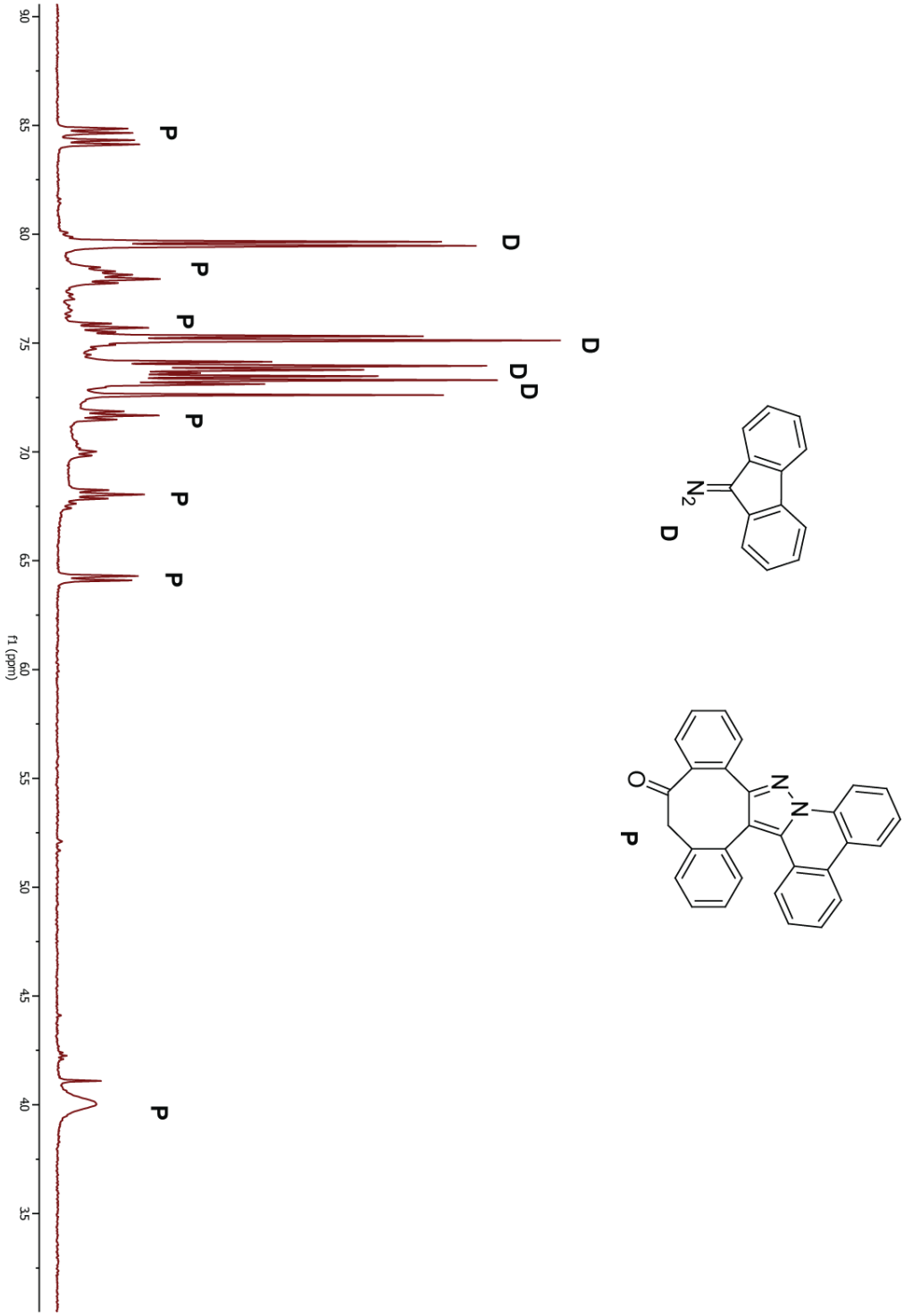
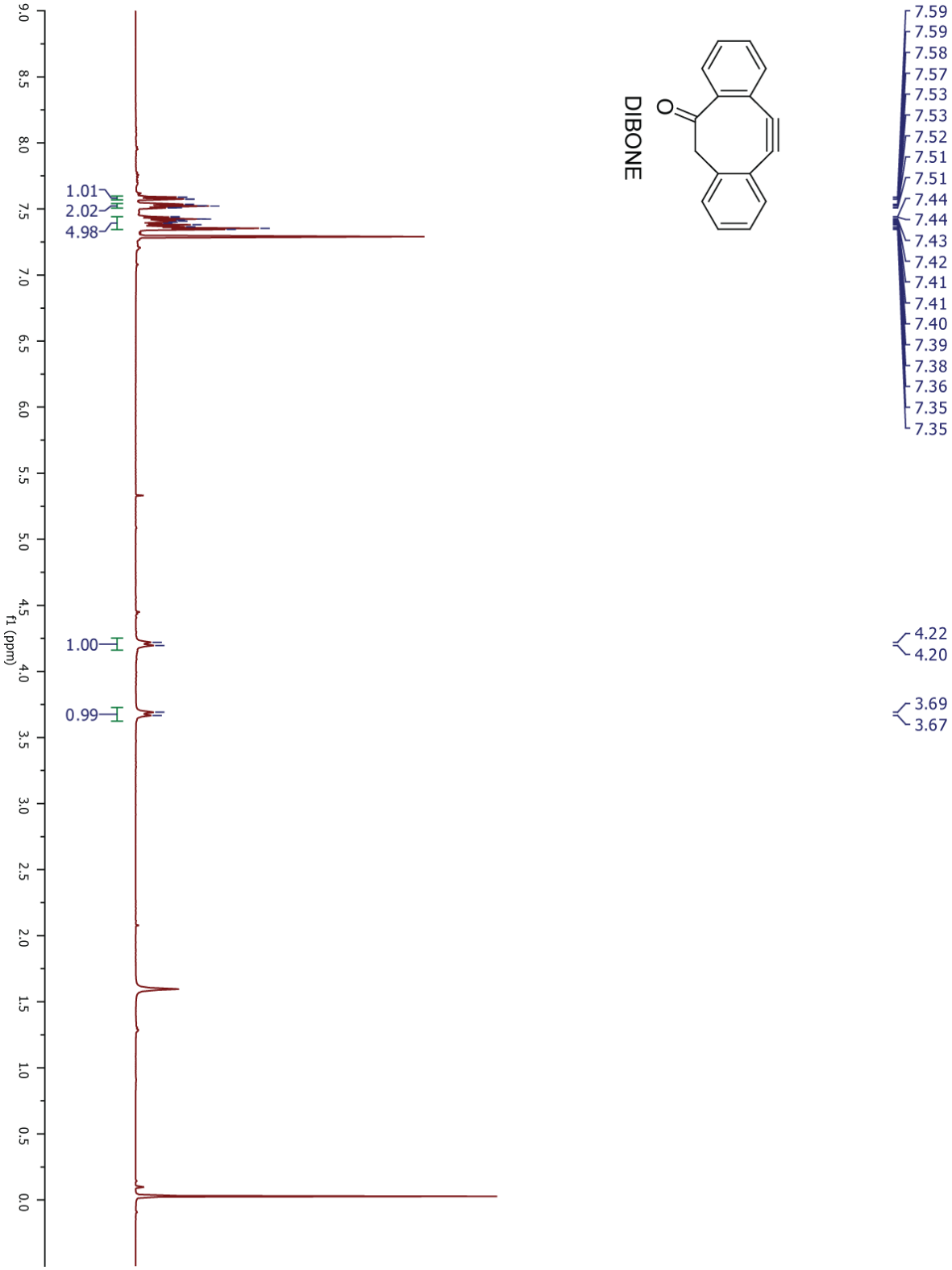
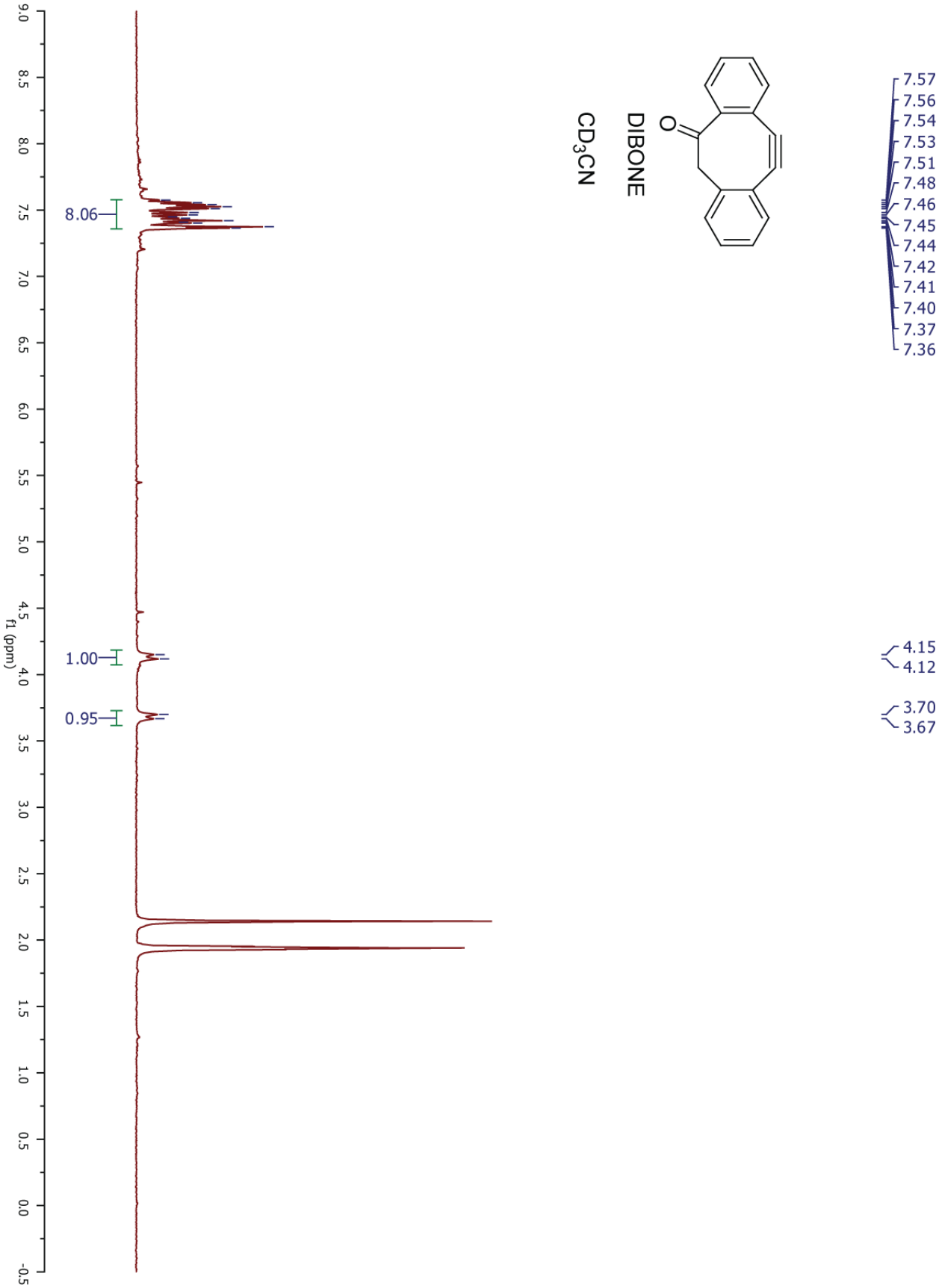
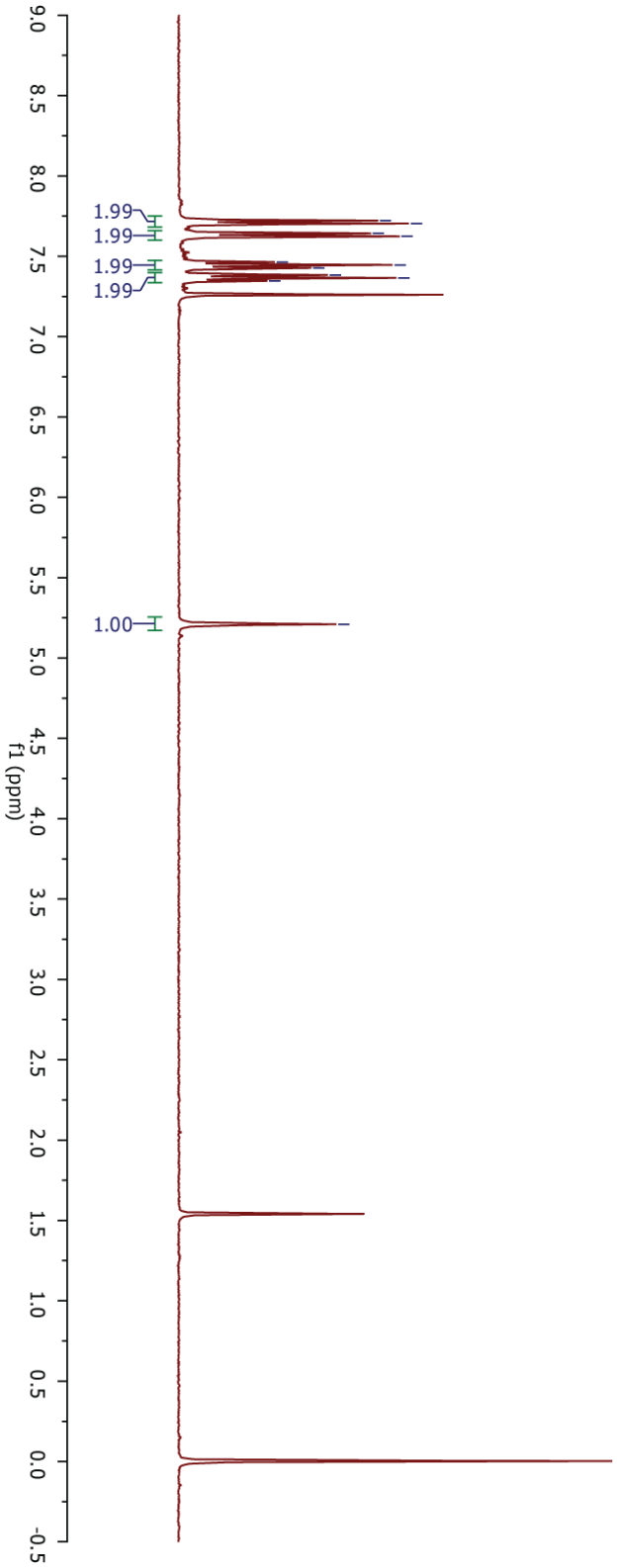


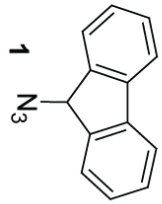
Fig. S5. Chemoselectivity Experiment: ^{1}H-NMR spectrum after treating a 2:1 acetonitrile:water solution (0.46 mL) of DIBONE (0.010 g, 0.046 mmol) and glutathione (0.140 g, 0.460 mmol) with diazofluorene **2** (0.026 g, 0.138 mmol) for 5 minutes, solvent was removed and the resulting residue dissolved in $CDCl_3$ for analysis. The reaction resulted in complete conversion of DIBONE to pyrazole (**P**) and the remaining 2 eq. of **2** were left unreacted.

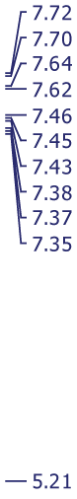
6. NMR Spectra (All compounds were dissolved in $CDCl_3$ unless indicated otherwise.)

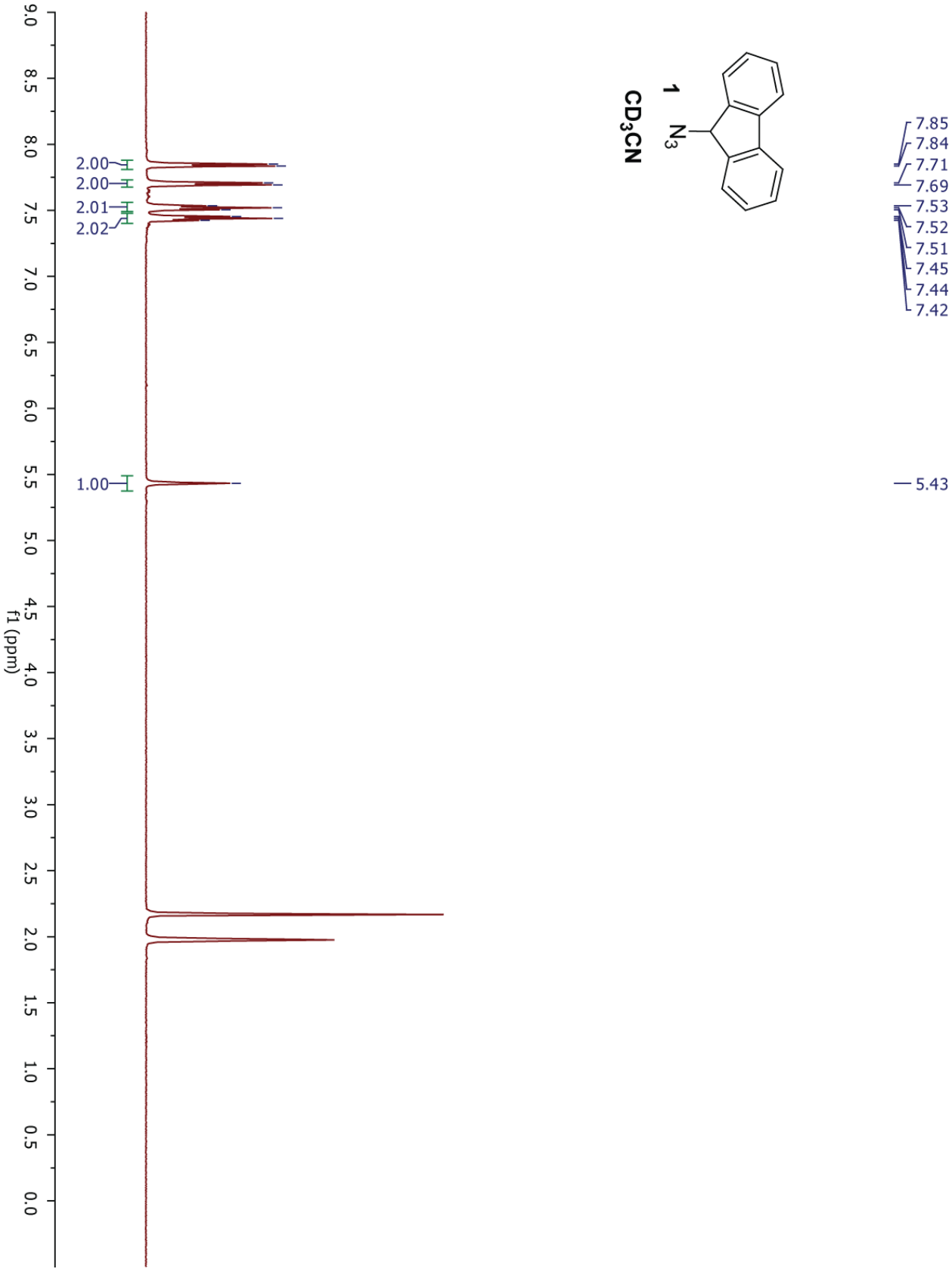


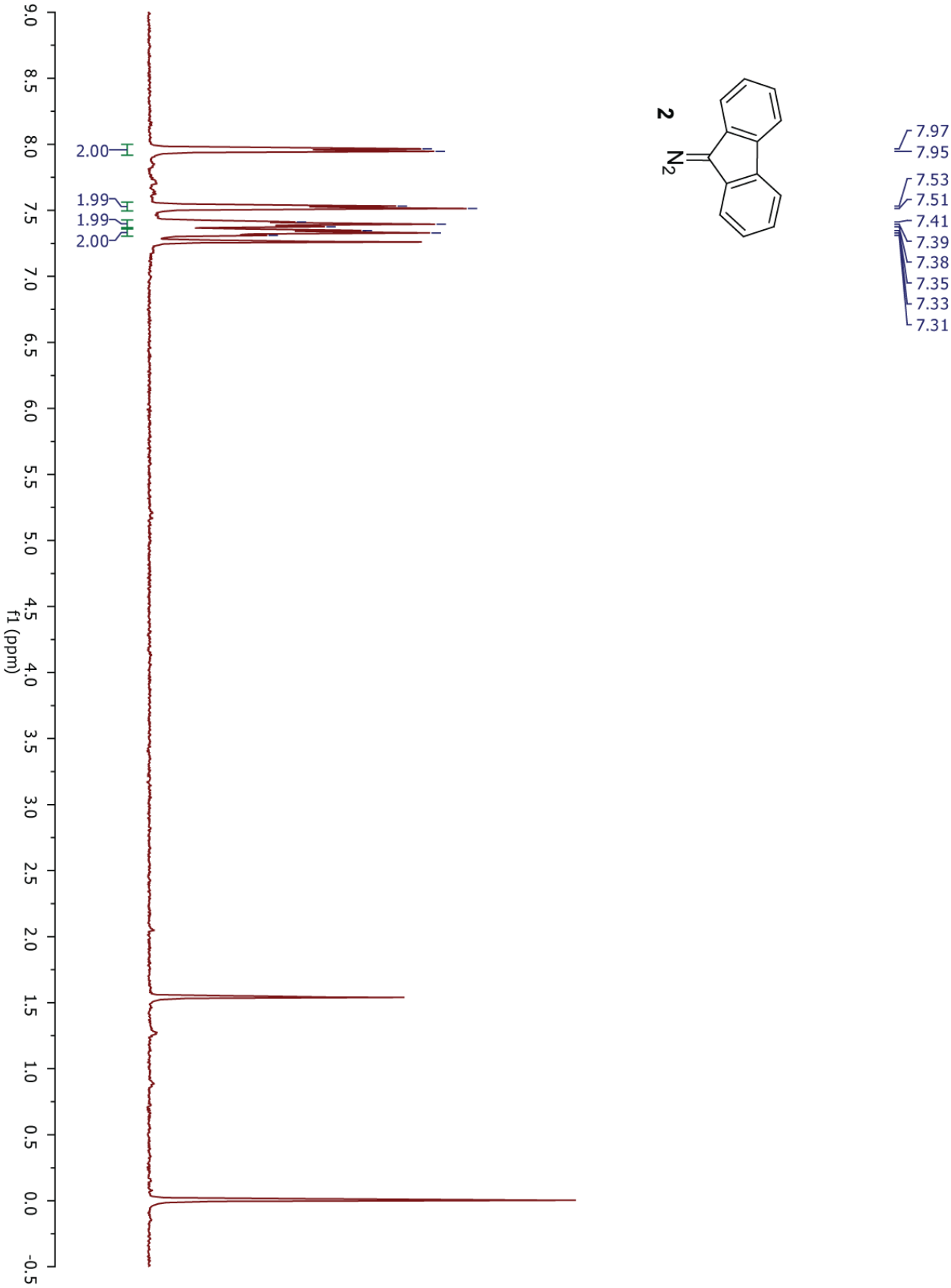


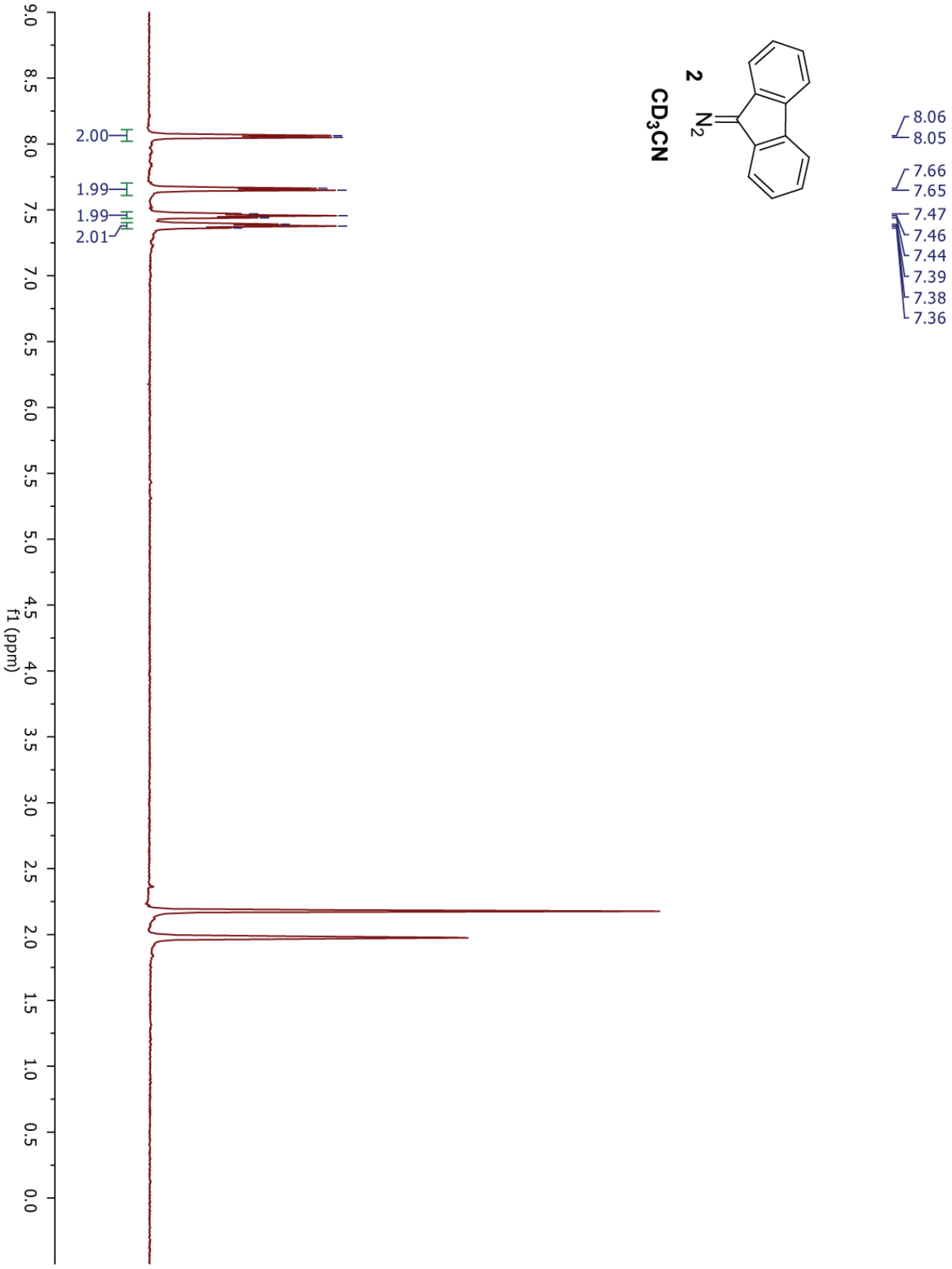


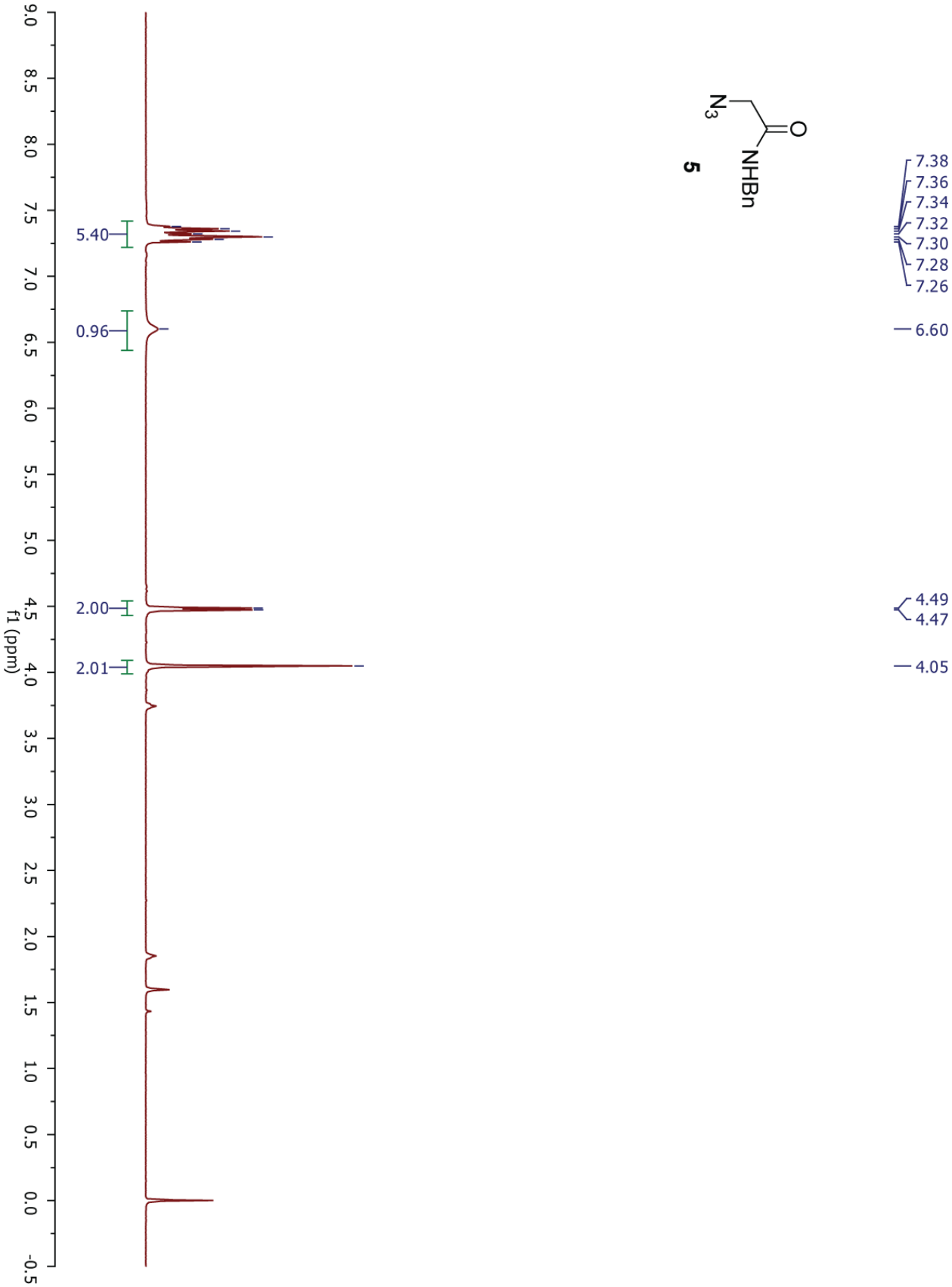


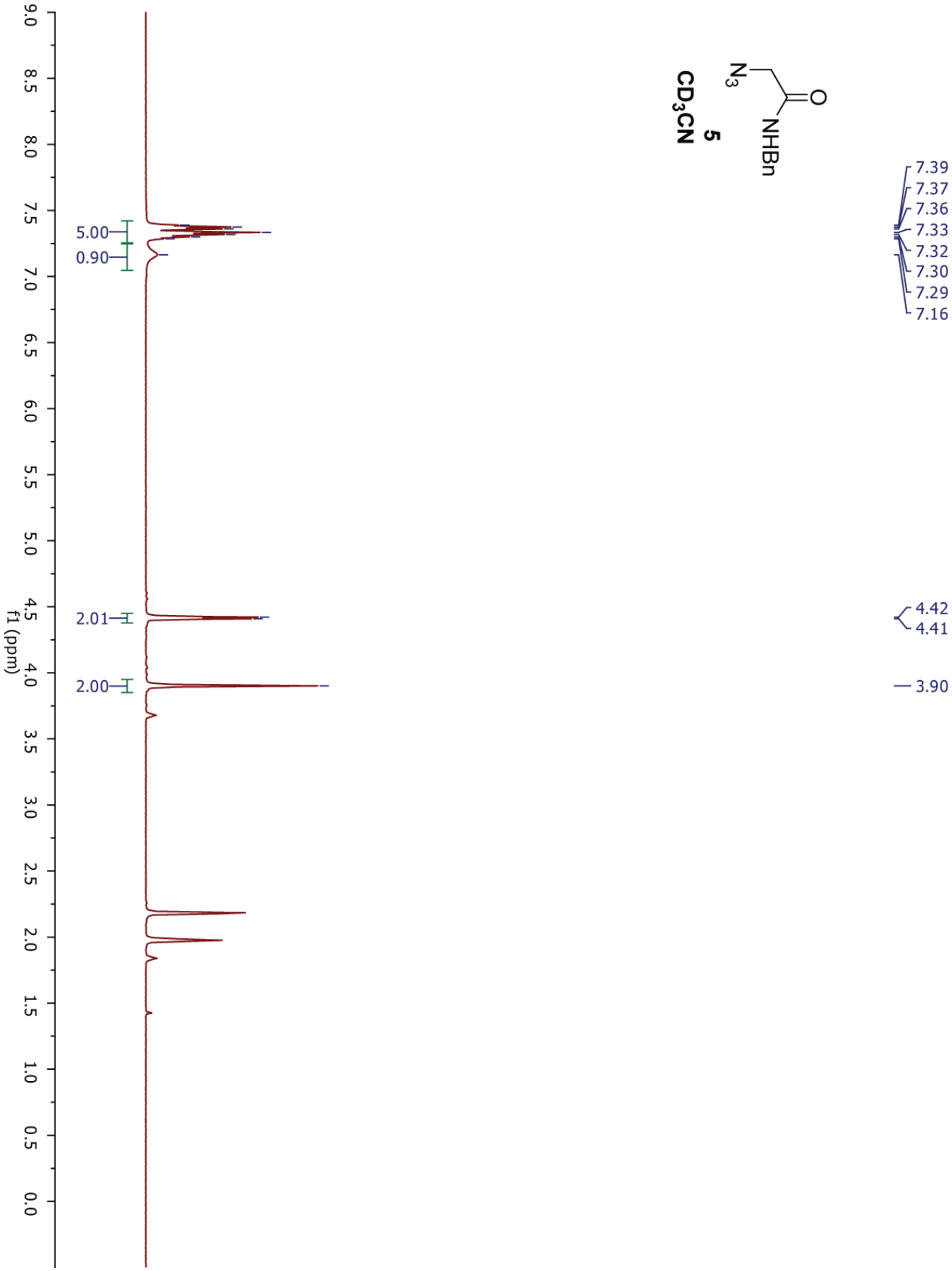


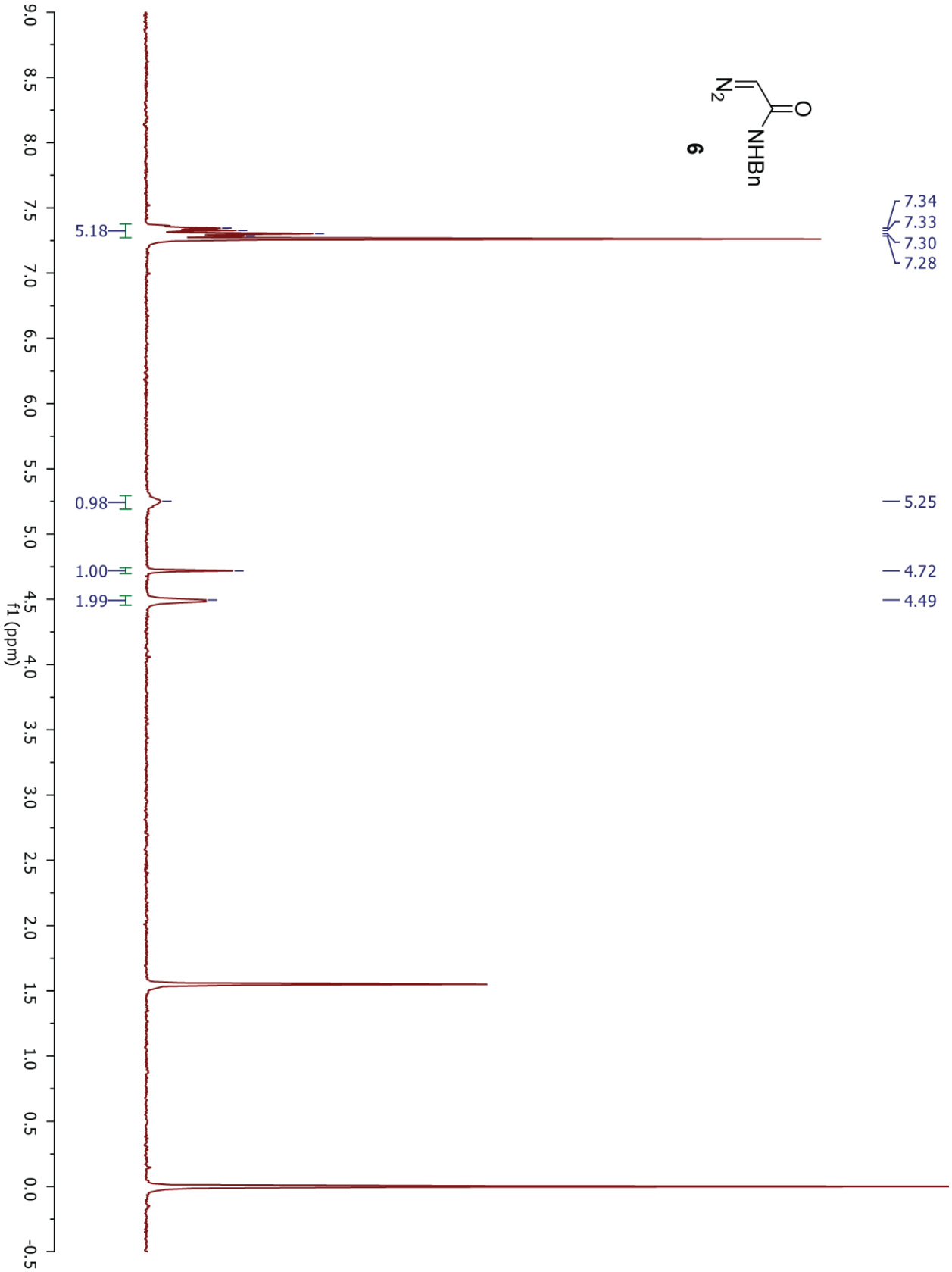


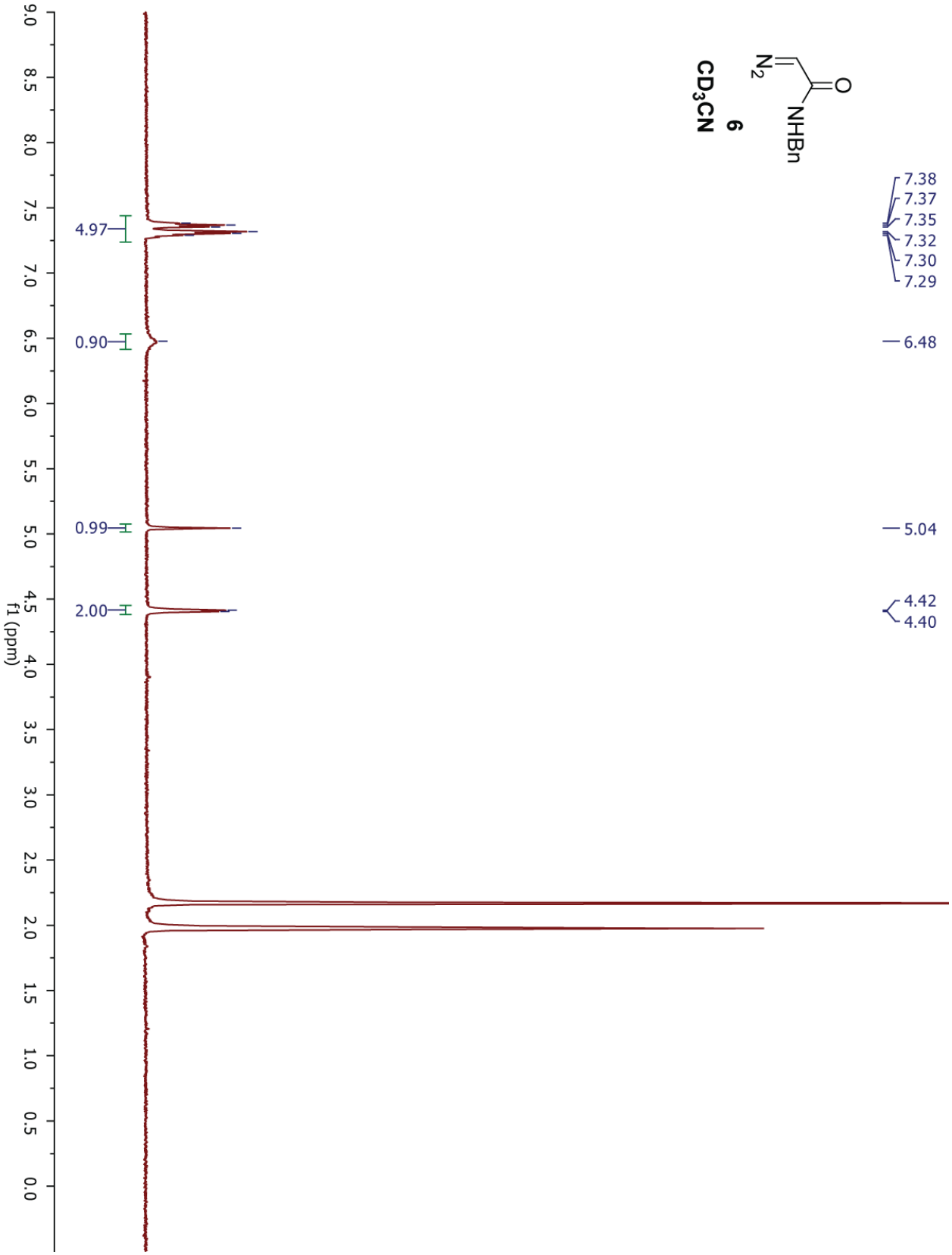


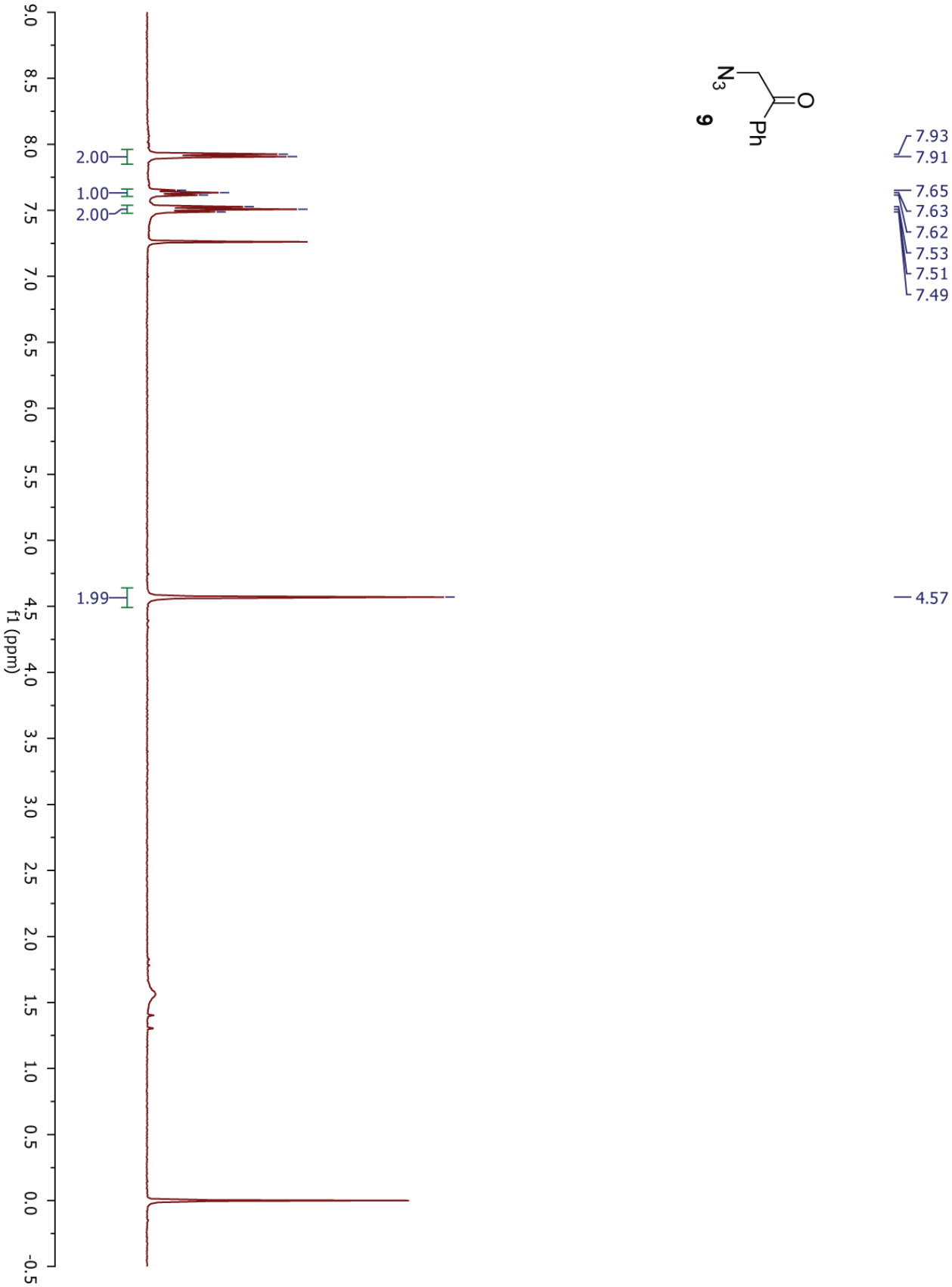


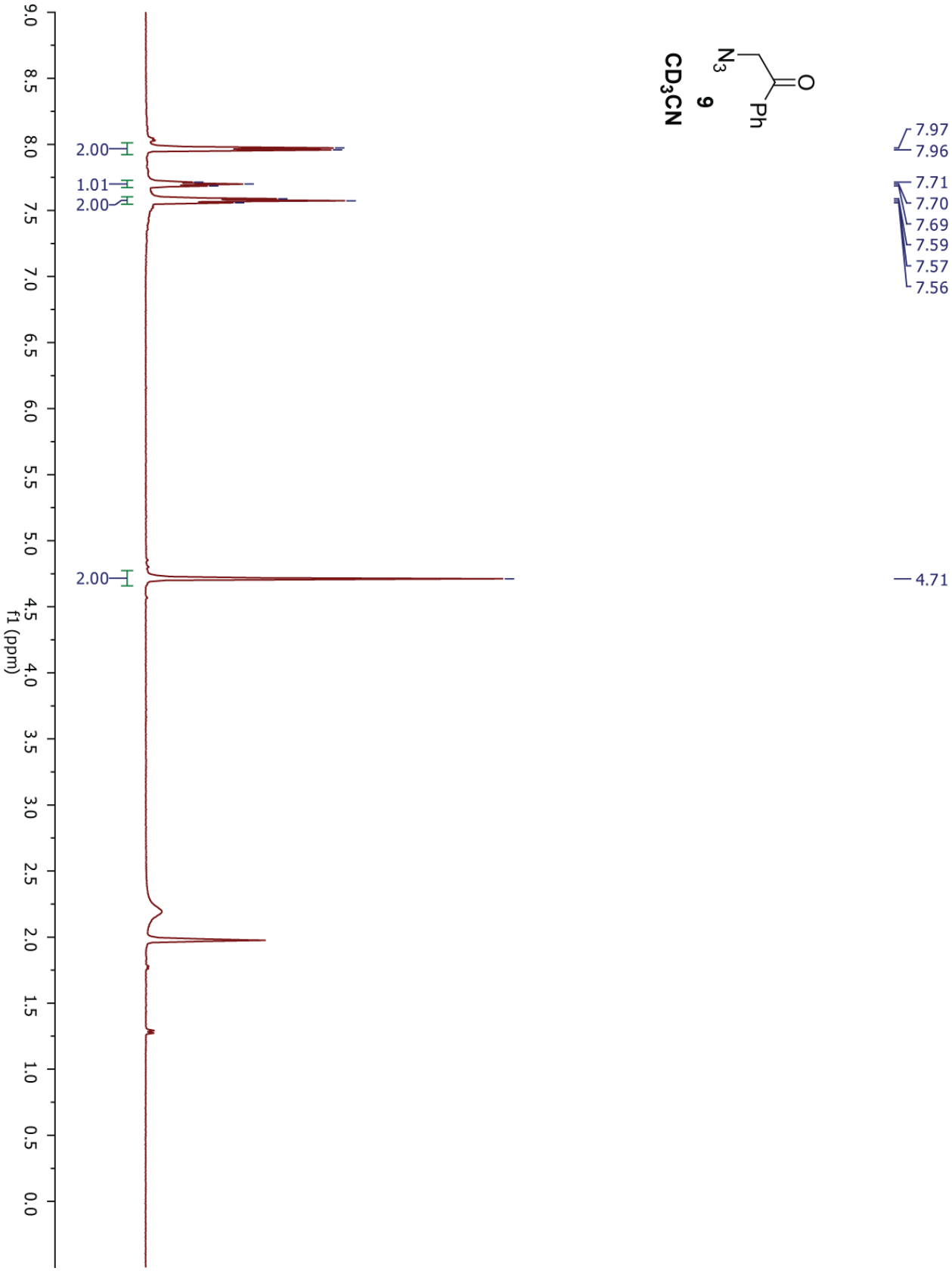


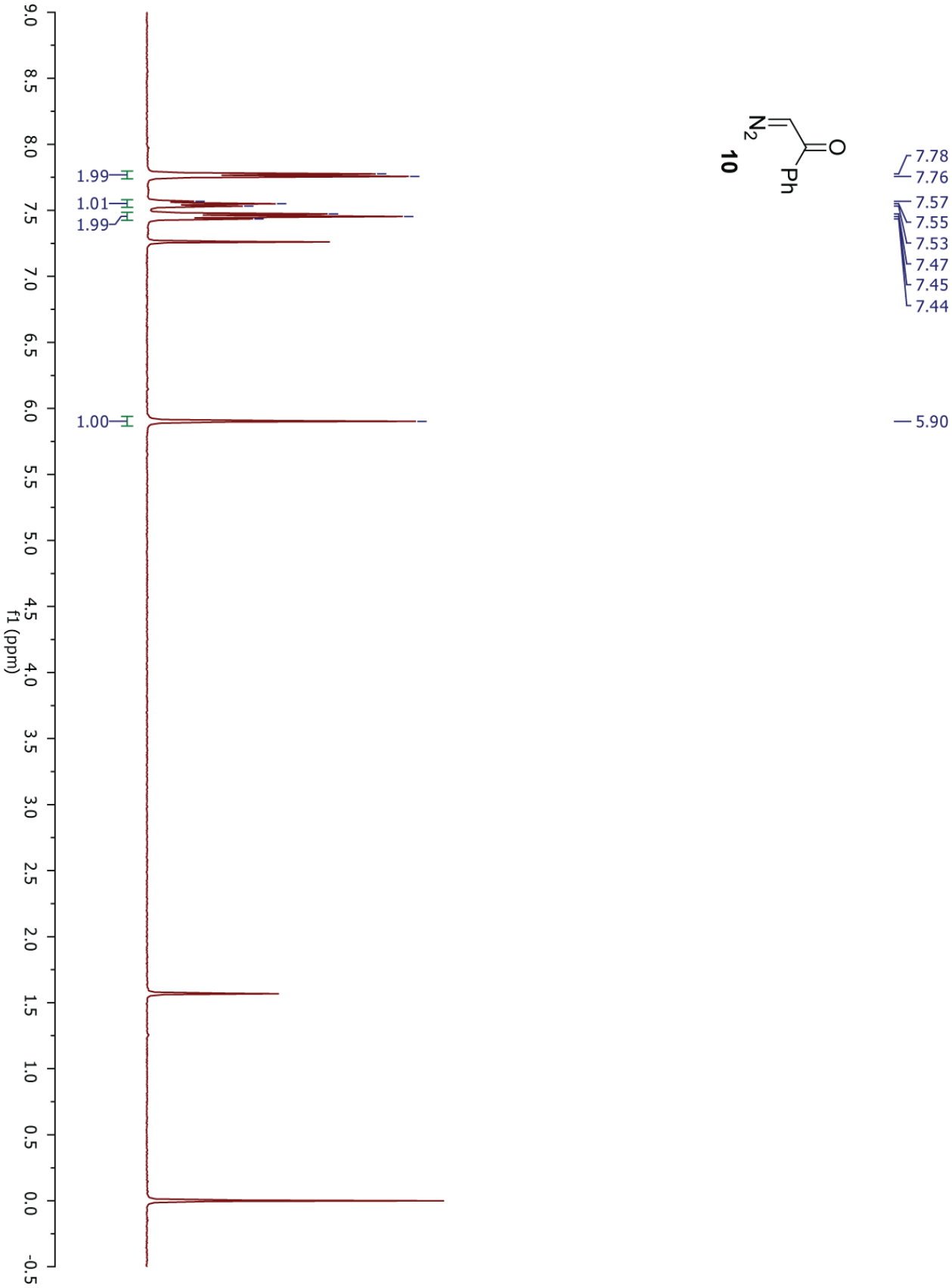


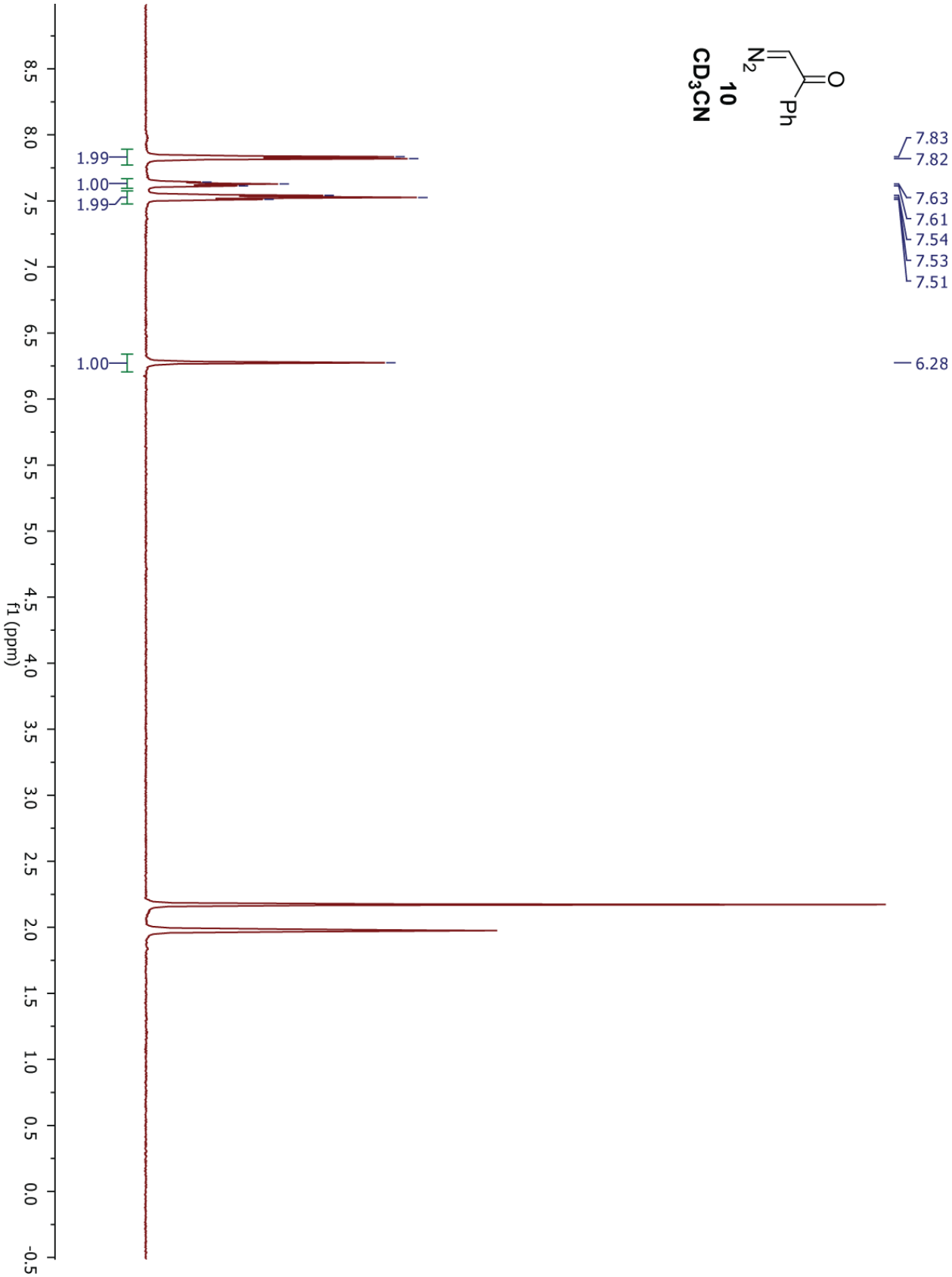


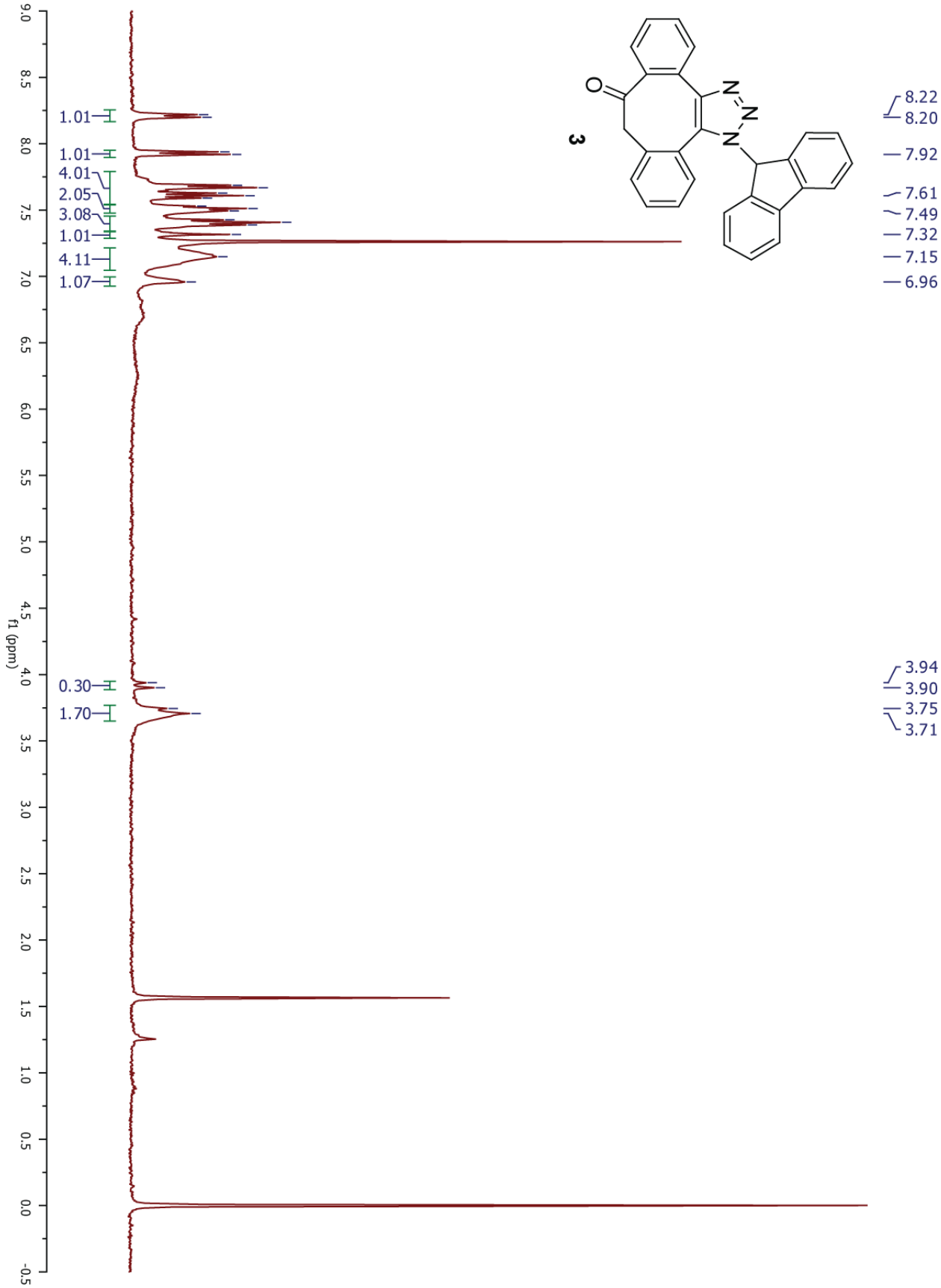


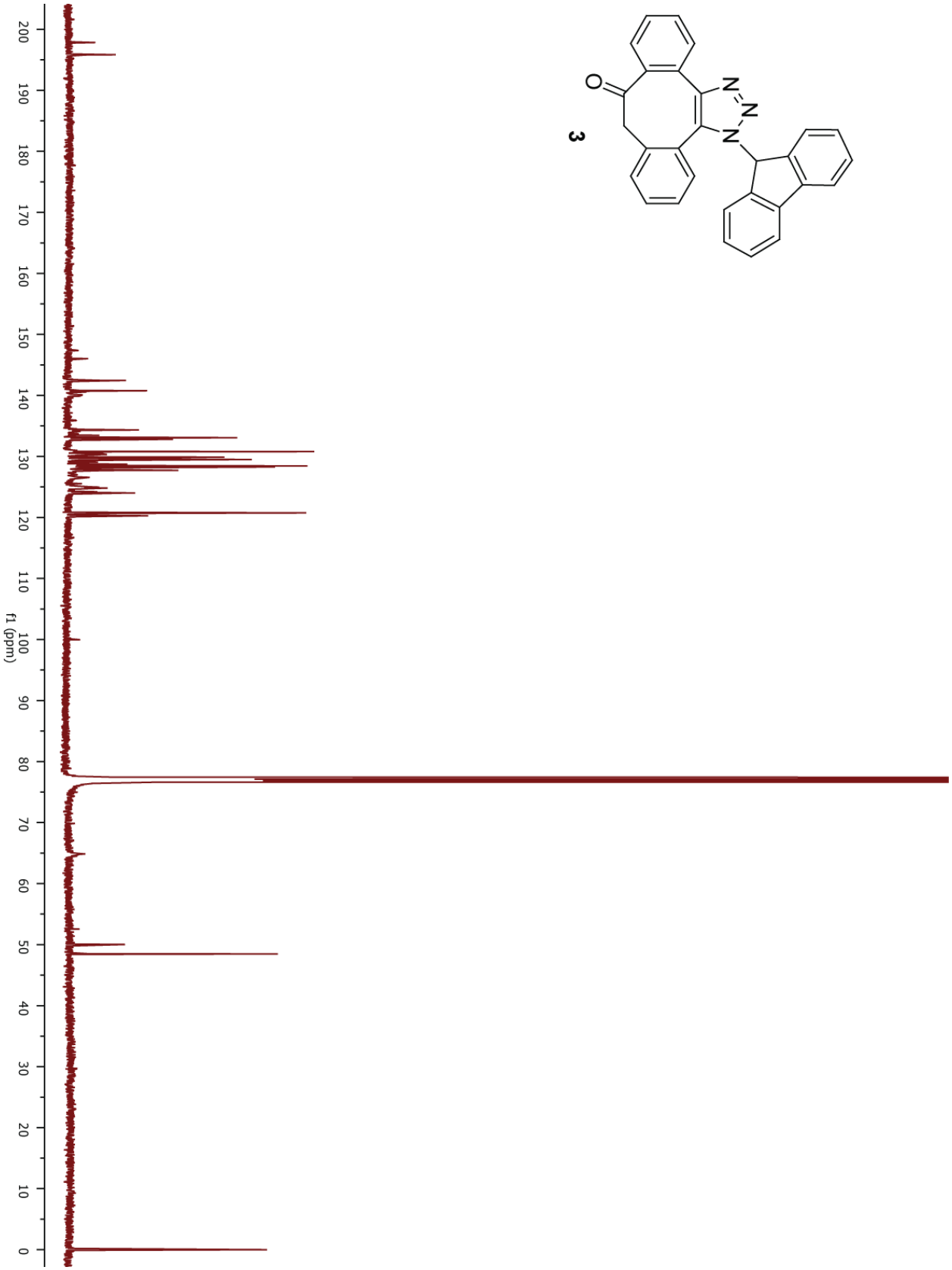


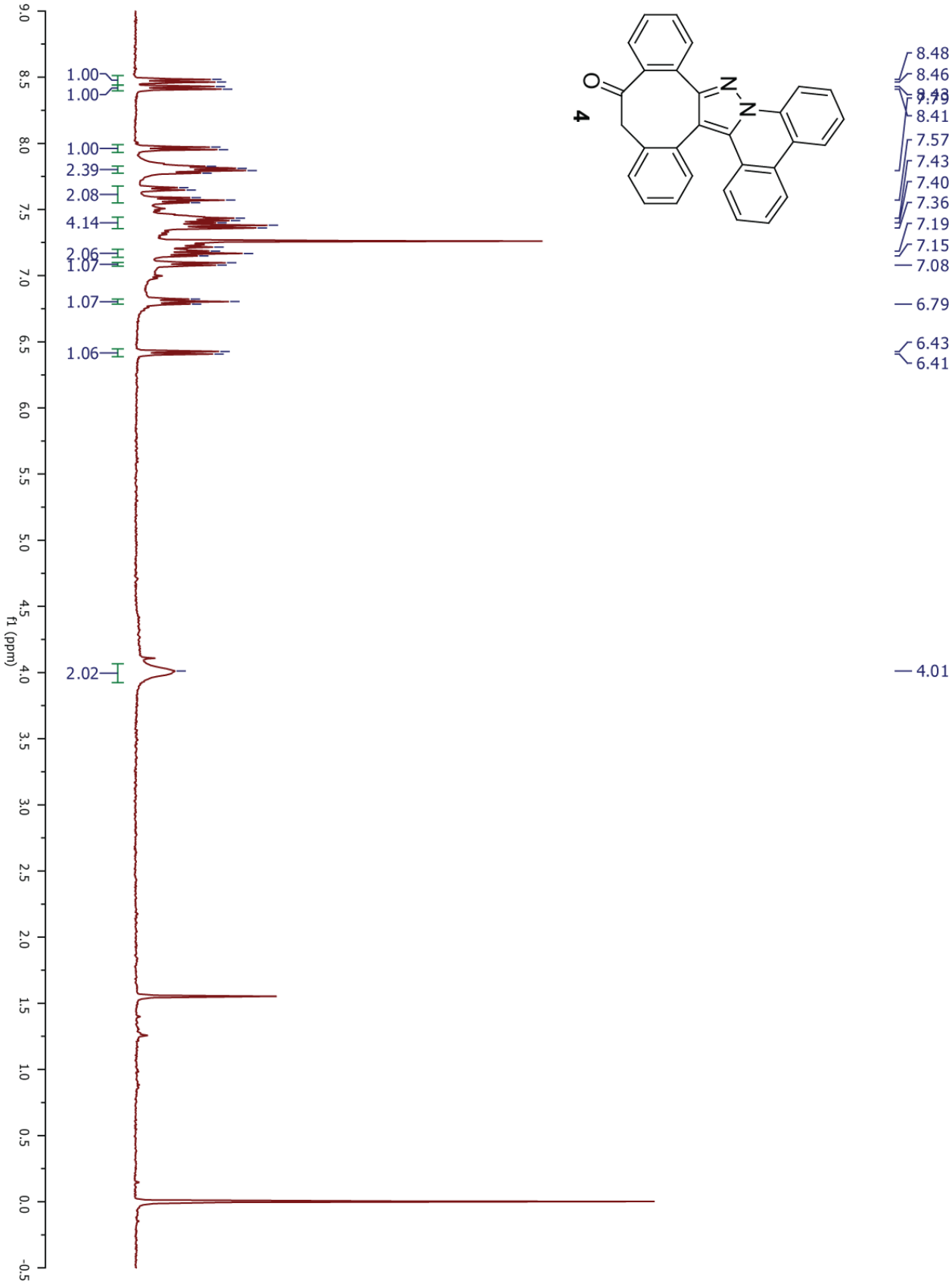


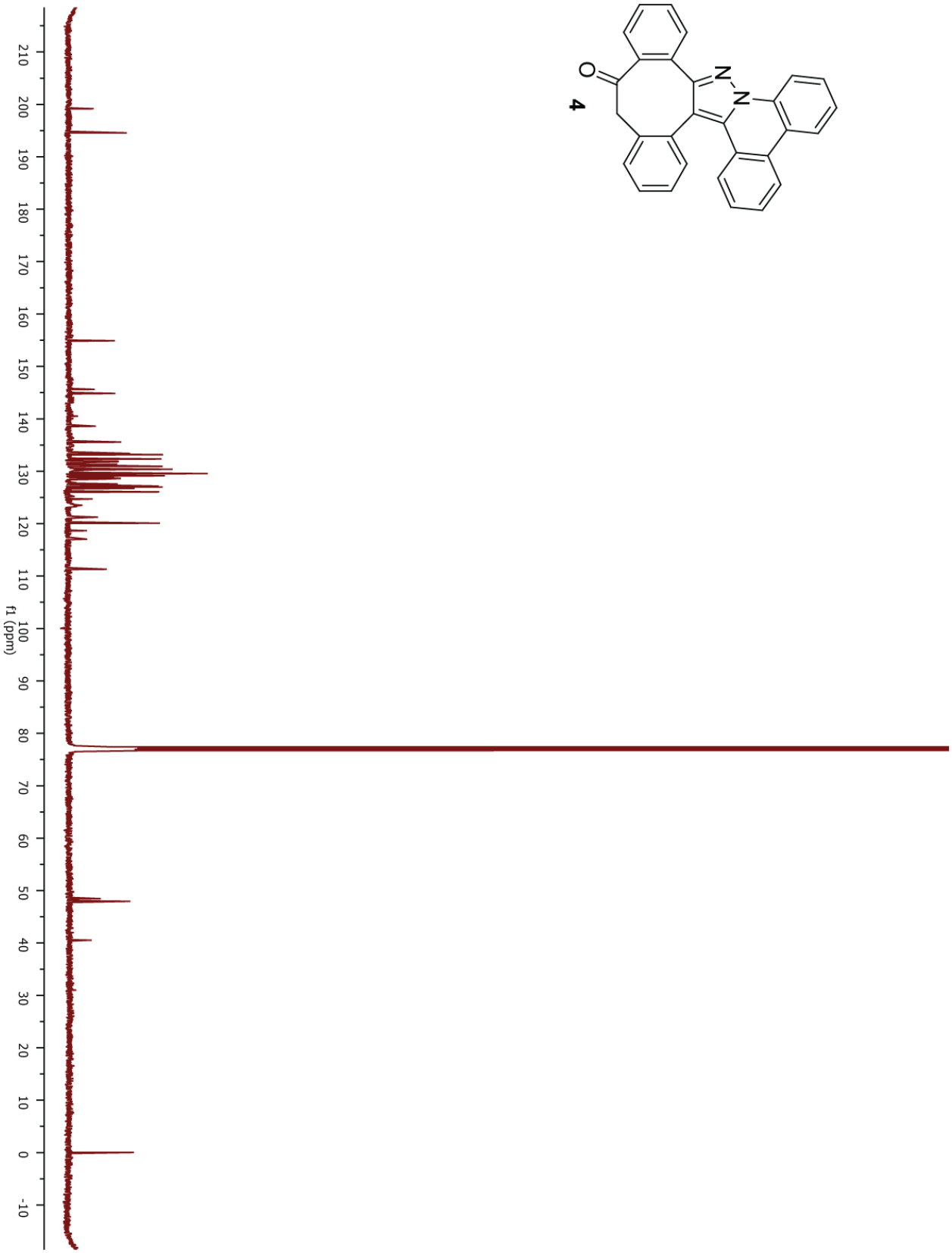


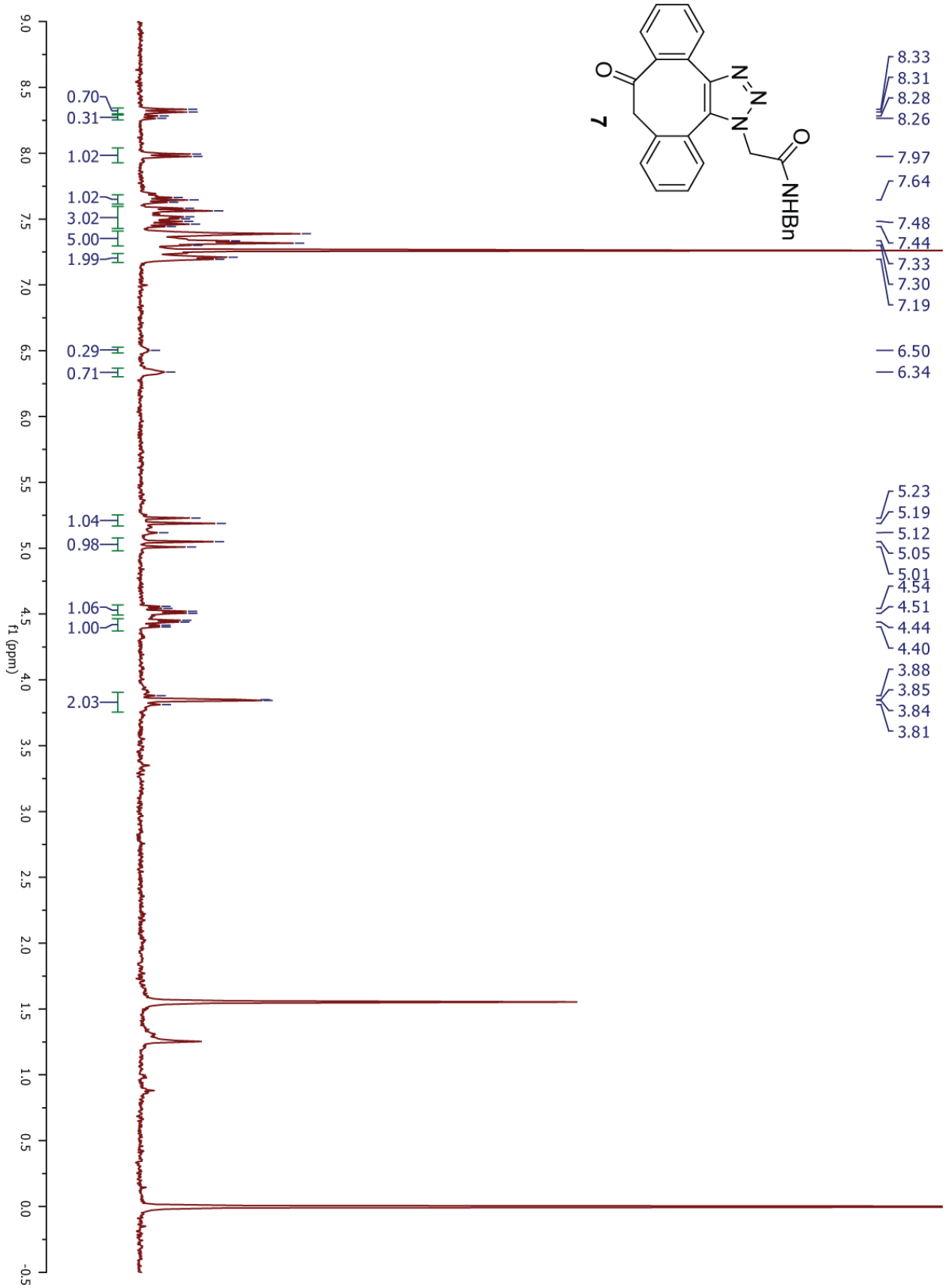


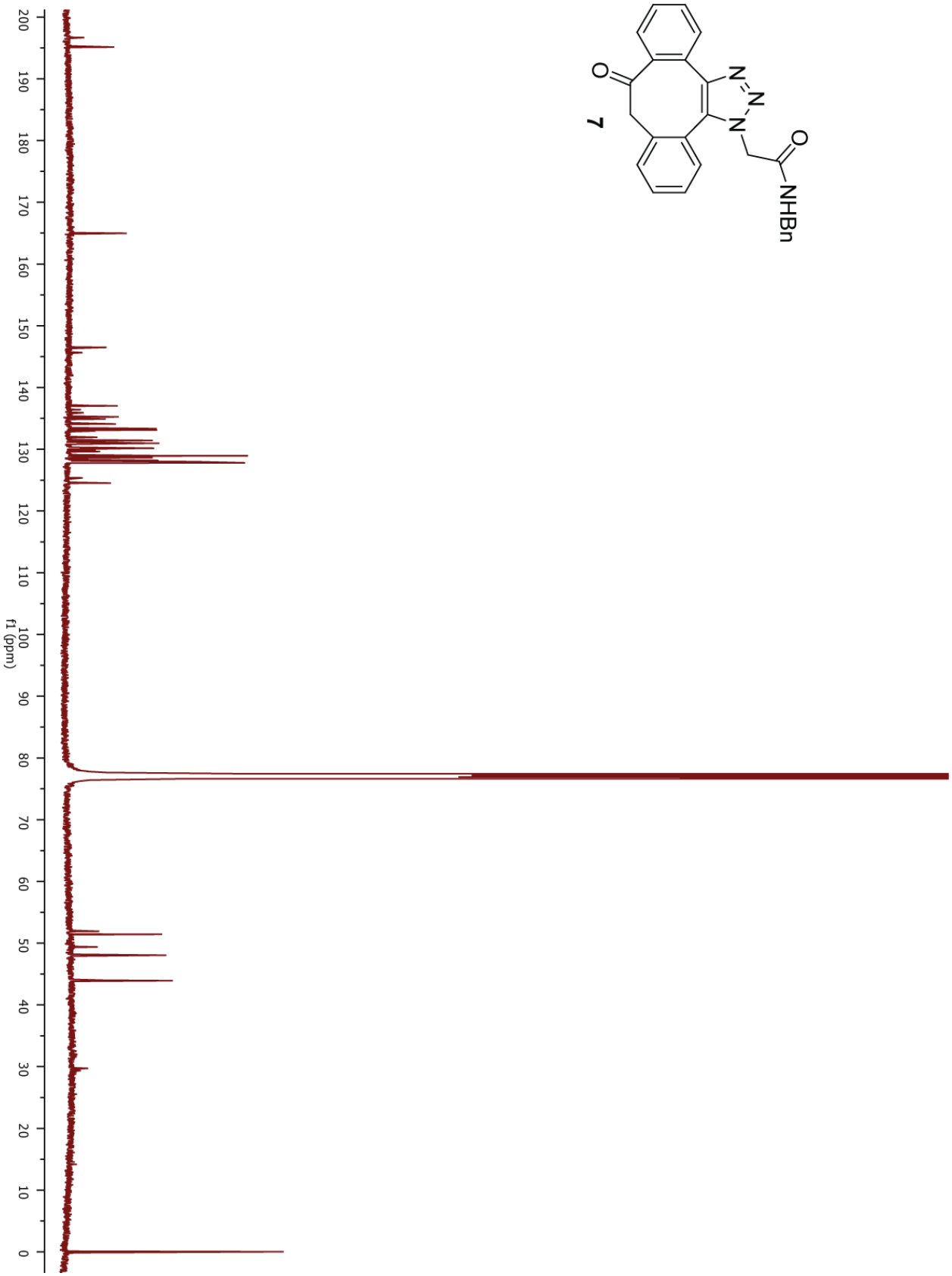


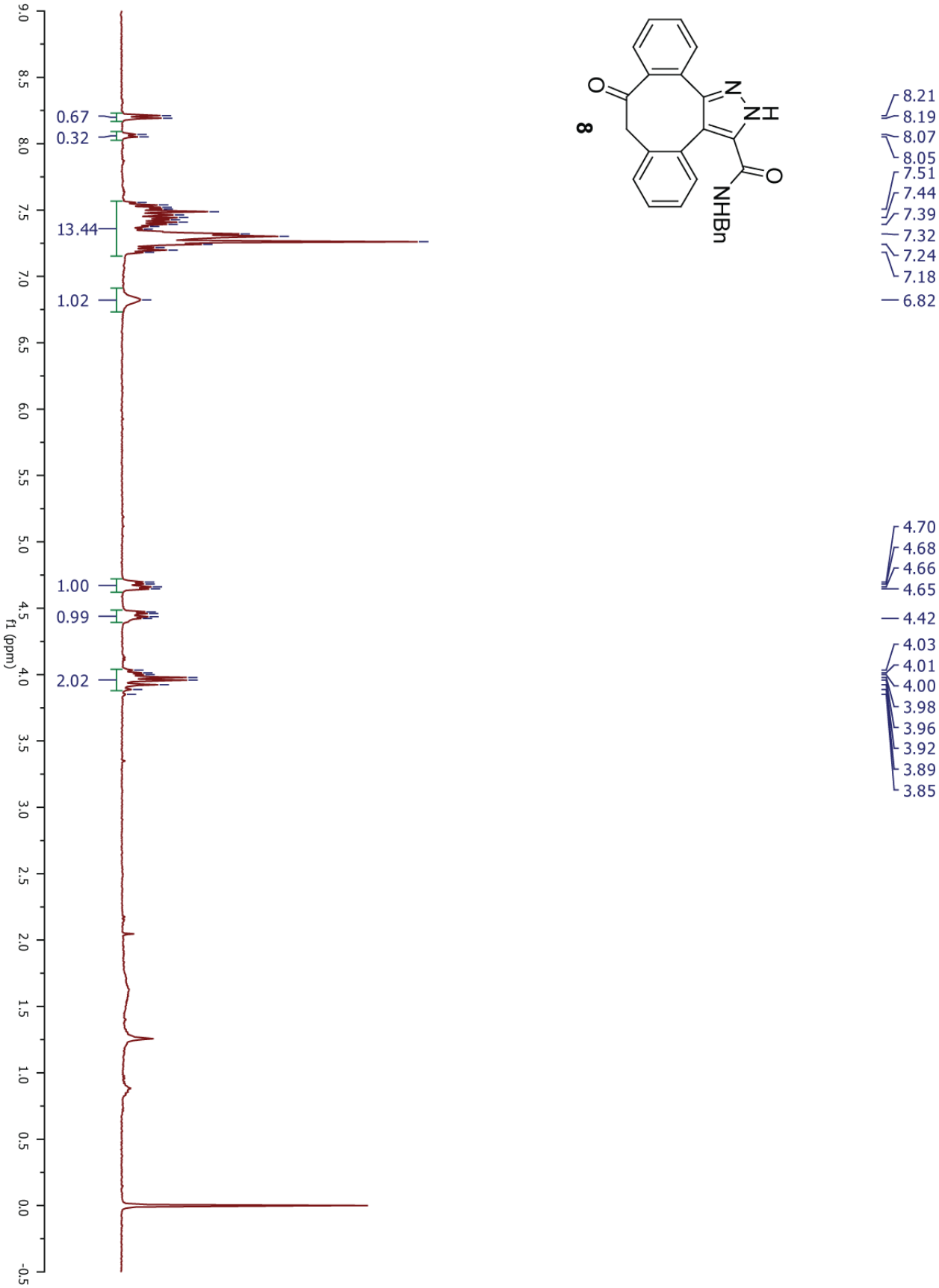


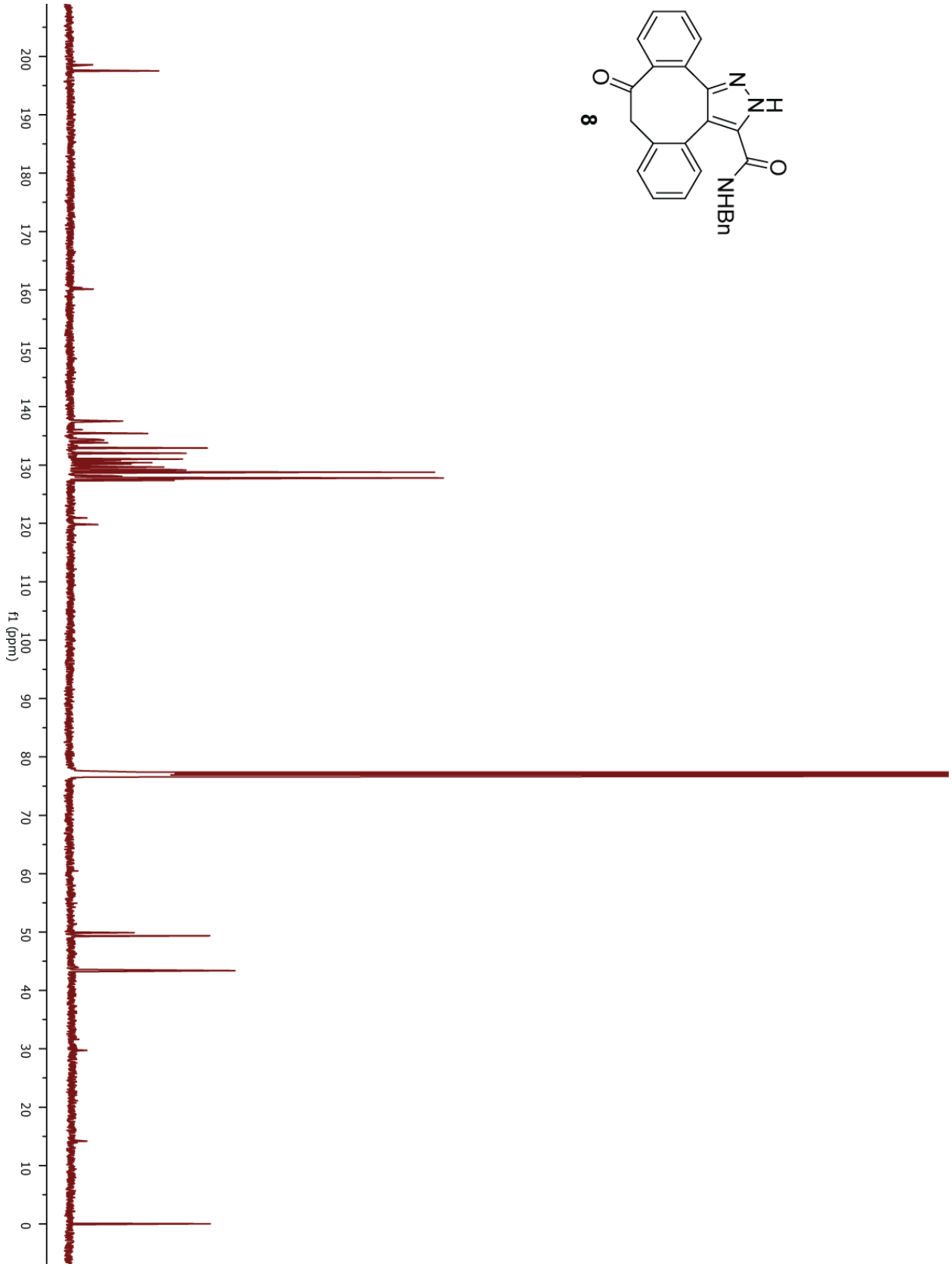












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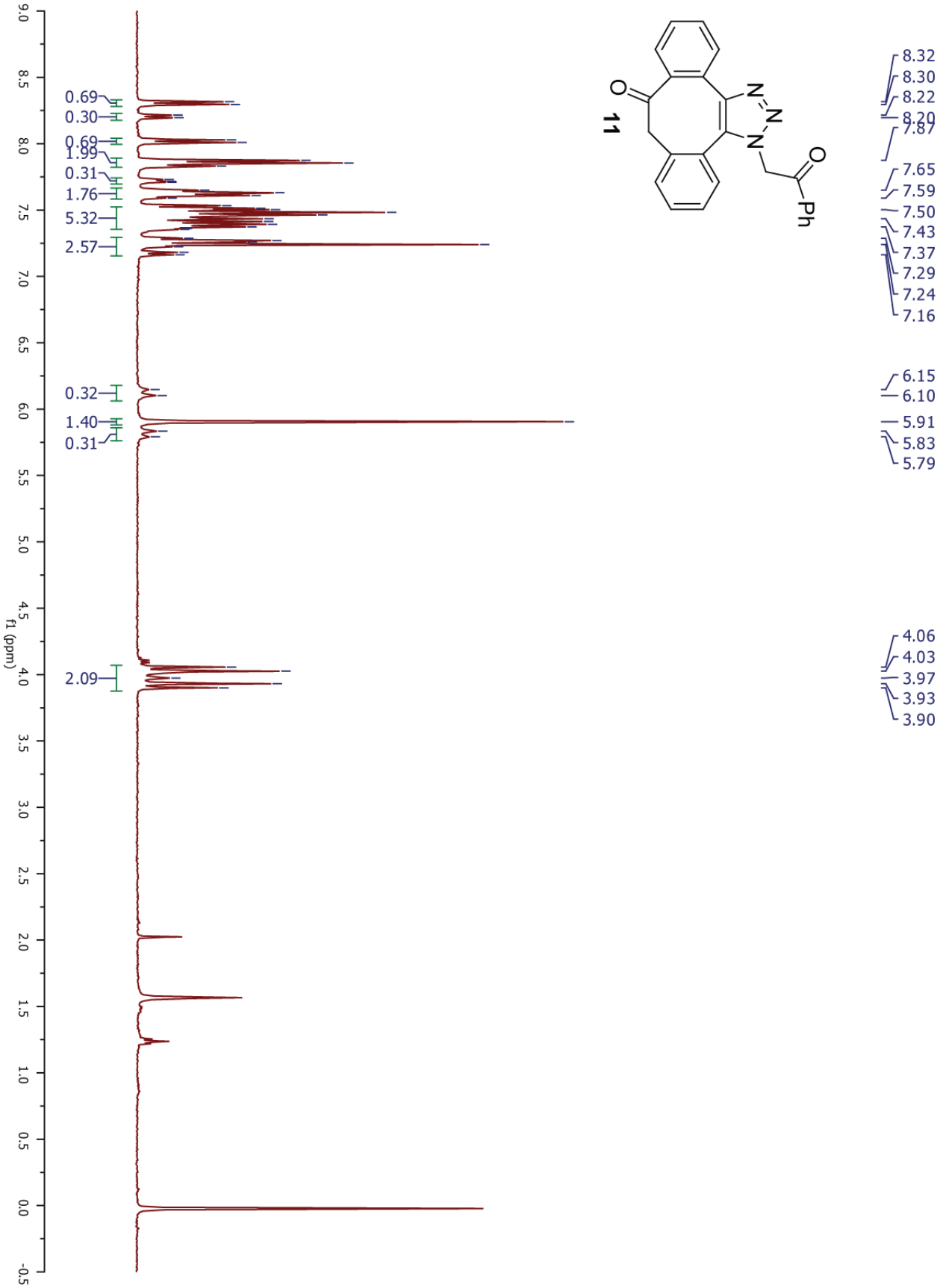

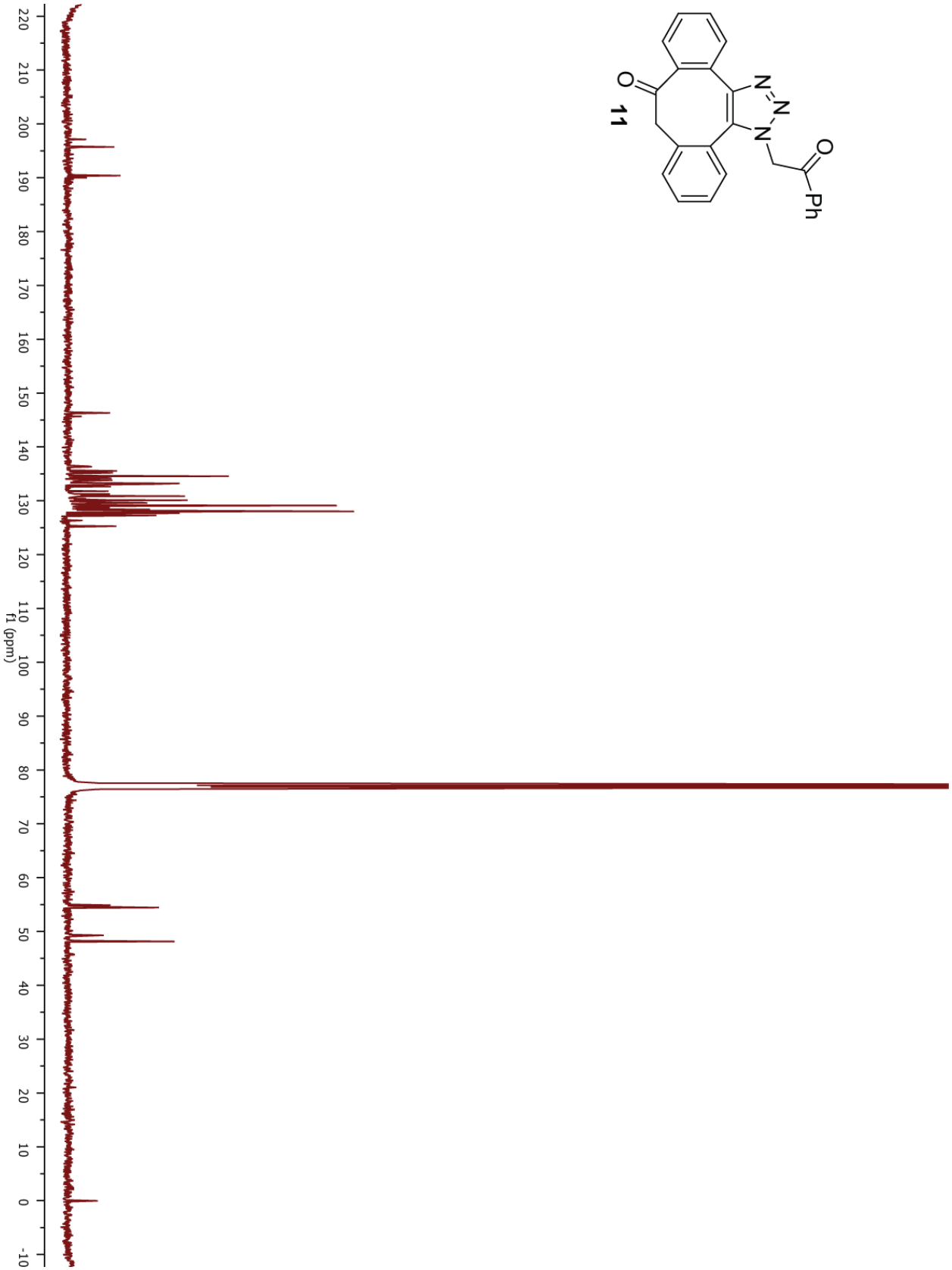

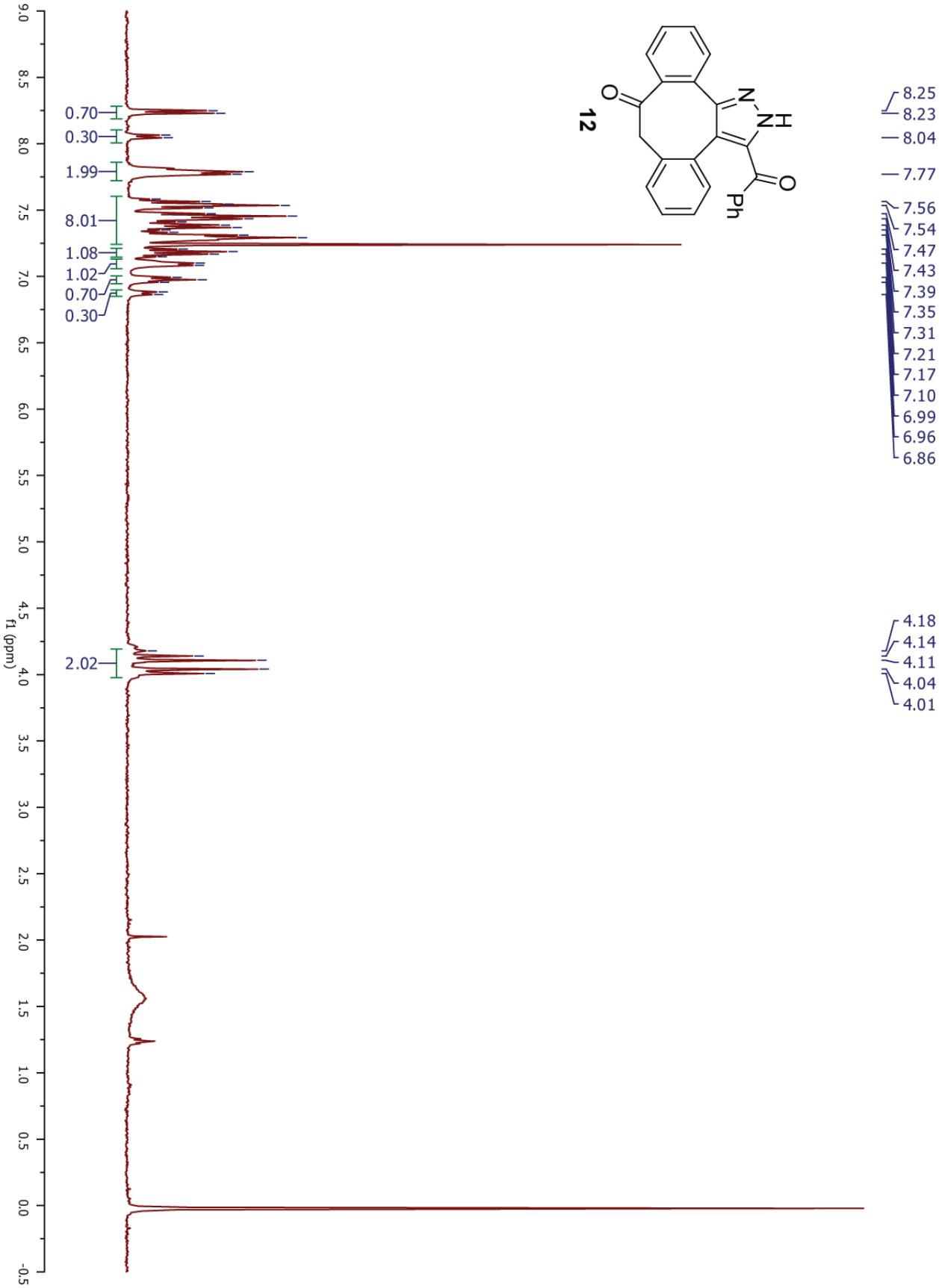

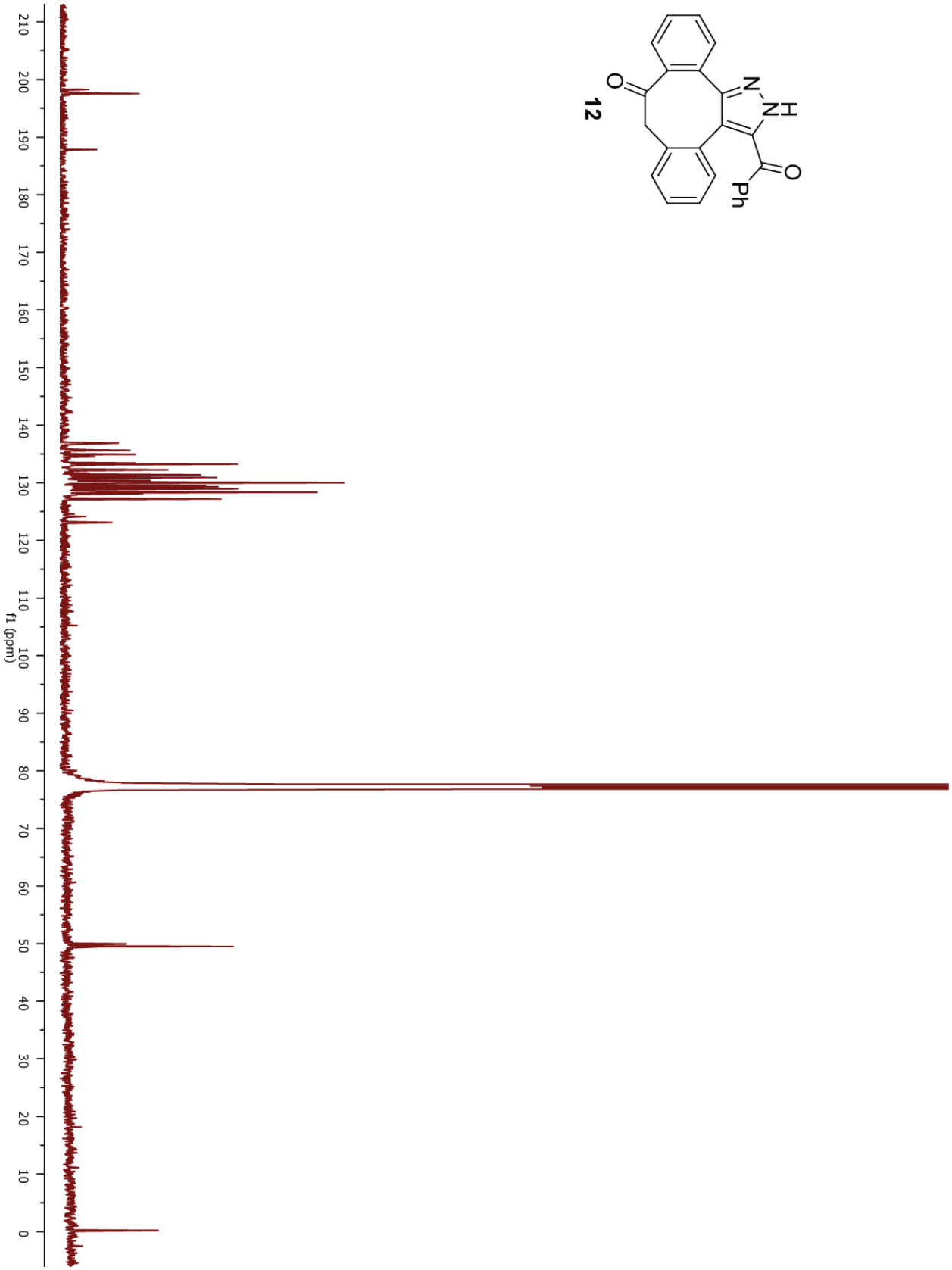

12

7. References

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