Supporting Information for:

The Benzil Rearrangement Reaction: Trapping of a Hitherto Minor Product and Its Application to the Development of a Selective Cyanide Anion Indicator

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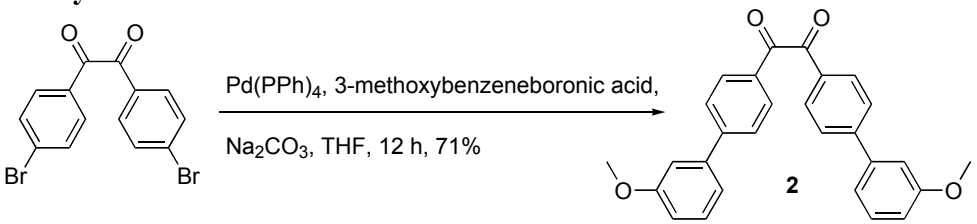
Contents

General Procedures

Proton and ^{13}C-NMR spectra were measured at 25 ºC using Varian Unity Innova instruments (400 or 500 MHz). UV-vis spectra were recorded on a Beckman DU 640B spectrophotometer. High resolution CI mass spectra were obtained on a VG ZAB2-E mass spectrometer. HPLC analyses were done using a LC-6AD Shimadzu system equipped with a SPD-M20A detector and an Eclipse XDB-C18 column.

Synthetic Experimental

Scheme 1. **Synthesis of Substrate 2**



Bis(4-(3-methoxyphenyl)phenyl)ethanedione (2)

Dibromobenzil (300 mg, 8.15×10^{-4} mol) and 3-methoxybenzeneboronic acid (272 mg, 1.79×10^{-3} mol) were added to one another in a 100 mL round bottom flask under argon. To the mixture, benzene (32 mL), ethanol (8 mL), water (16 mL), and Na_2CO_3 (0.345 g, 3.26×10^{-3} mol) were added and degassed for 10 min. Tetrakis(triphenylphosphine)palladium(0) (56 mg, 4.89×10^{-4} mol, 6 mol%) was added and the resulting mixture was stirred at 80 °C under an argon atmosphere overnight. The reaction mixture was poured into water and extracted with dichloromethane. The organic layer was washed with brine, dried over anhydrous sodium sulfate, and evaporated to dryness under reduced pressure. The residue obtained was purified by column chromatography over silica gel (ethyl acetate : hexane = 1:4, eluent) to afford **2** (244 mg, 71%) as a yellow solid.

^{1}H-NMR (400 MHz, $CDCl_3$) [ppm]: 3.87 (s, 6H), 6.95 (m, 2H), 7.15 (s, 2H), 7.21 (d, J = 8.0 Hz, 2H), 7.39 (dd, J = 8.0, 8.0 Hz, 2H), 7.23 (d, J = 8 Hz, 2H), 8.06 (d, J = 8 Hz, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$) [ppm]: 55.36, 113.14, 113.90, 119.81, 127.72, 130.07, 130.49, 131.81, 140.97, 147.47, 160.05, 194.09. HRMS (CI): m/z 423.1593 ((M+H), calcd for $C_{28}H_{23}O_4$ 423.1596.

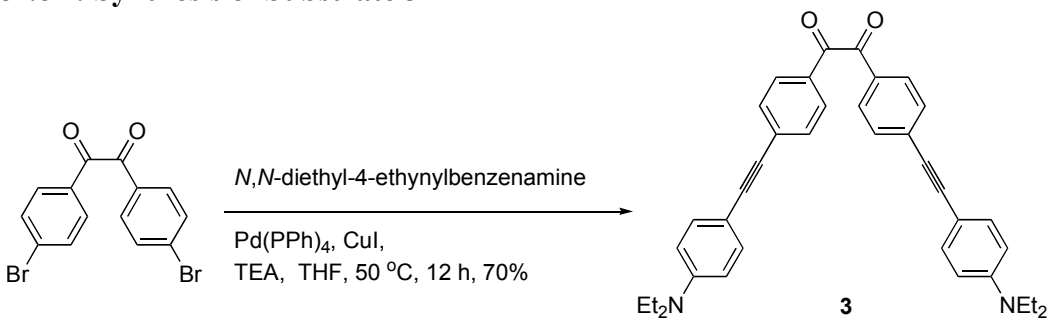
Cyano(4-(3-methoxyphenyl)phenyl)methyl 4-(3-methoxyphenyl)benzoate (2a)

Diketone **2** (20 mg, 4.73×10^{-5} mol) was added to a 25 mL round bottom flask and dissolved in 6 mL of $CHCl_3$. Tetrabutylammonium cyanide (25 mg, 9.46×10^{-5} mol in 1 mL $CHCl_3$) was added and the reaction mixture was stirred for 20 min at room temperature. The resulting solution was evaporated to dryness under reduced pressure. The residue obtained was directly purified by column chromatography over silica gel (ethyl acetate : hexane = 1:4, eluent) to afford **2a** (17 mg, 80%).

^{1}H-NMR (400 MHz, $CDCl_3$) [ppm]: 3.87 (s, 6H), 6.74 (s, 1H), 6.95 (m, 2H), 7.13 (m, 2H), 7.19 (m, 2H), 7.39 (ddd, J = 8.0, 8.0, 2.4 Hz, 1H), 7.68 (m, 6H), 8.14 (d, J = 8.8 Hz, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$) [ppm]: 55.61, 63.41, 113.28, 113.37, 113.53, 113.95,

116.45, 119.93, 120.01, 127.11, 127.62, 128.30, 128.62, 130.23, 130.29, 130.87, 131.11, 141.33, 141.63, 143.59, 146.99, 160.26, 160.29, 164.77. HRMS (CI): m/z 450.1704 (M+H), calcd for $C_{29}H_{24}NO_4$ 450.1705.

Scheme 2. **Synthesis of Substrate 3**



Bis(4-((4-(diethylamino)phenyl)ethynyl)phenyl)ethanedione (3)

A mixture of dibromobenzil (100 mg, 2.70×10^{-4} mol), *N,N*-diethyl-4-ethynylbenzenamine (94 mg, 5.40×10^{-4} mol), tetrakis(triphenylphosphine)palladium(0) (18 mg, 8.10×10^{-6} mol), and CuI (6 mg, 1.62×10^{-5} mol) in TEA (3 mL) and THF (40 mL) were degassed for 10 min. The solution was stirred at 50 °C under an argon atmosphere overnight. The resulting mixture was evaporated to dryness and redissolved in ethyl acetate and washed with water. The organic layer was separated off, dried over anhydrous sodium sulfate, and evaporated to dryness under reduced pressure. The residue obtained was purified by column chromatography over silica gel (ethyl acetate : hexane = 1:4, eluent) to afford **3** (104 mg, 70%) as a red solid.

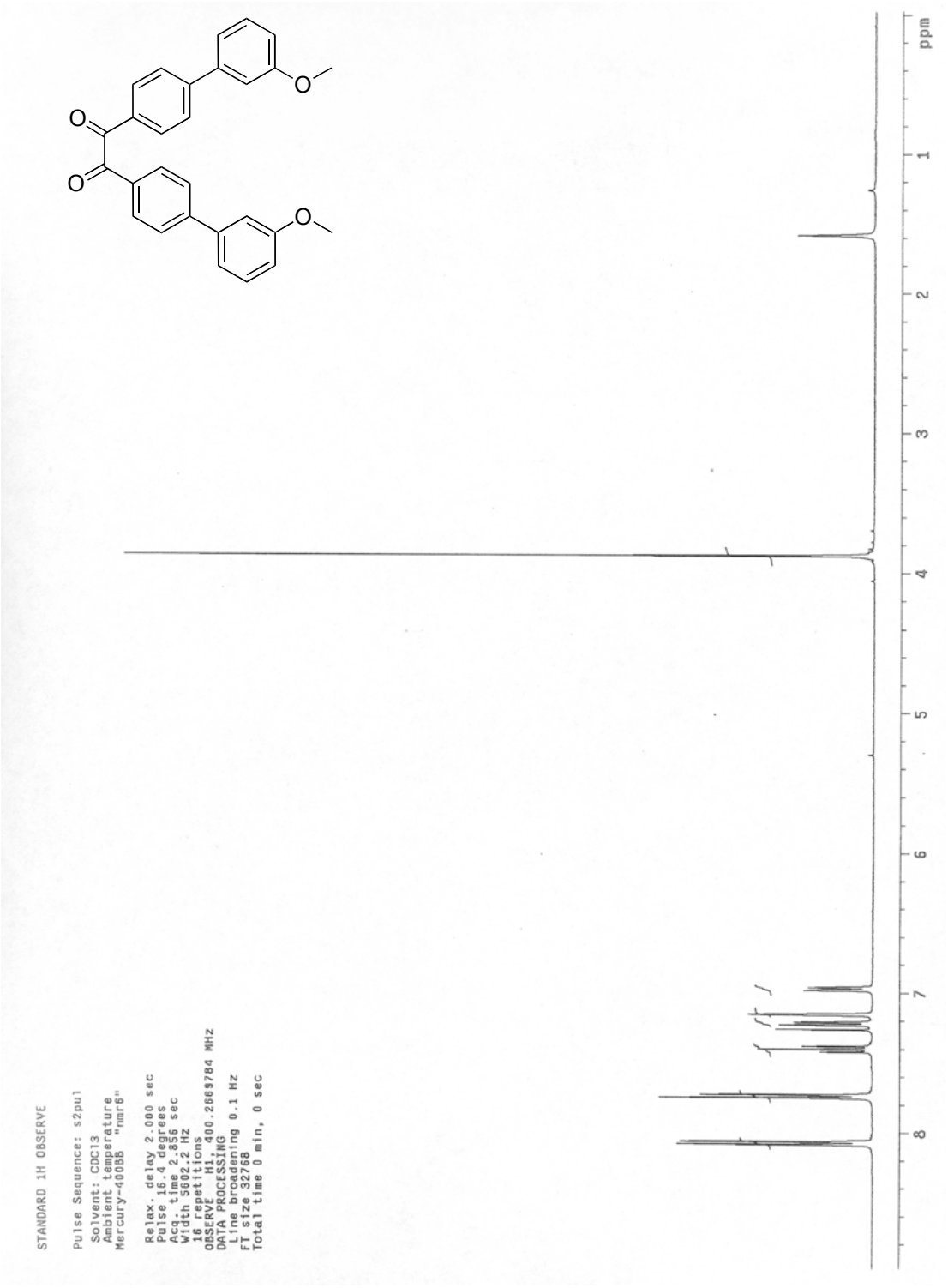
^{1}H-NMR (400 MHz, $CDCl_3$) [ppm]: 1.18 (t, J = 7.2 Hz, 12H), 3.37 (q, J = 7.2 Hz, 4H), 6.61 (d, J = 4.0 Hz, 4H), 7.39 (d, J = 4.0 Hz, 4H), 7.57 (d, J = 8.4 Hz, 4H), 7.92 (d, J = 8.4 Hz, 4H). ^{13}C-NMR (100 MHz, $CDCl_3$) [ppm]: 12.53, 44.35, 87.11, 96.71, 107.21, 111.06, 129.81, 130.98, 131.38, 131.44, 133.40, 148.08, 193.57. HRMS (CI): m/z 553.2853 (M+H), calcd for $C_{38}H_{37}N_2O_2$ 553.2855.

Cyano(4-((4-(diethylamino)phenyl)ethynyl)phenyl)methyl 4-((4-(diethylamino) phenyl)ethynyl)benzoate (3a)

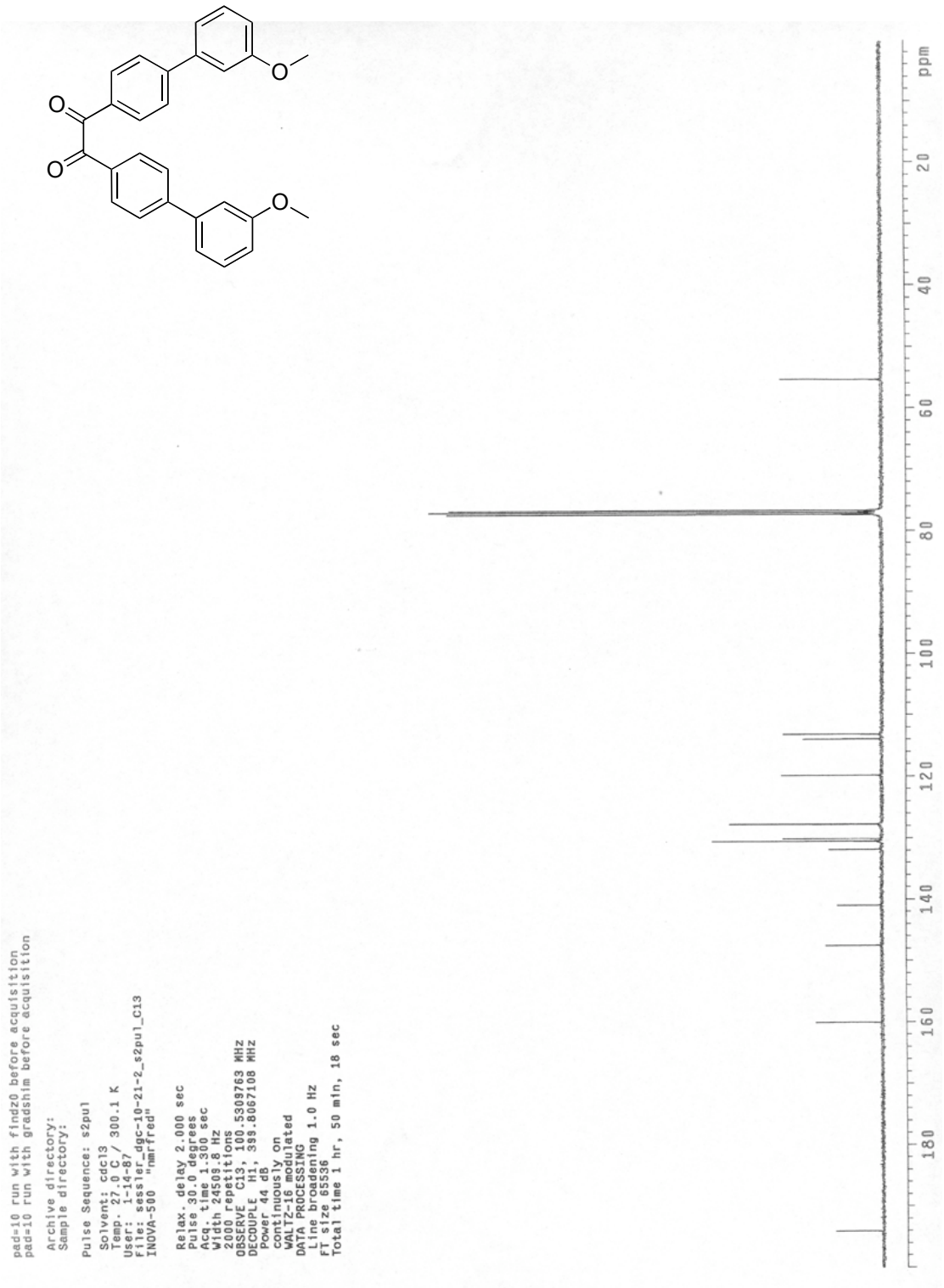
Diketone **3** (20 mg, 3.61×10^{-5} mol) was added to a 25 mL round bottom flask and dissolved in 6 mL of $CHCl_3$. Tetrabutylammonium cyanide (11.6 mg, 4.32×10^{-5} mol in 1 mL $CHCl_3$) were added and stirred at room temperature for 20 min. The resulting solution was evaporated to dryness under reduced pressure. The residue obtained was directly purified by column chromatography over silica gel (ethyl acetate : hexane = 1:4, eluent) to afford **2a** (14 mg, 67%).

^{1}H-NMR(400 MHz, $CDCl_3$) [ppm]: 1.18 (t, J = 6.8 Hz, 12H), 3.38 (q, J = 6.8 Hz, 8H), 6.62 (d, J = 4.8 Hz, 4H), 6.65 (s, 1H), 7.38 (d, J = 4.8 Hz, 4H), 7.56 (m, 6H), 8.00 (d, J = 4.8 Hz, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$) [ppm]: 12.53, 44.33, 63.10, 86.20, 86.75, 93.17, 95.66, 107.78, 108.10, 111.09, 111.12, 116.02, 126.02, 126.87, 127.83, 129.95, 130.57, 131.12, 131.85, 133.12, 133.30, 147.79, 147.99, 164.26. HRMS (CI): m/z 580.2969 (M+H), calcd for $C_{39}H_{38}N_3O_2$ 580.2964. Anal. Calcd for $C_{39}H_{37}N_3O_2$: C, 80.80; H, 6.43; N, 7.25; Found C, 80.60; H; 6.39; N, 7.26.

NMR Spectra



^{1}H NMR spectrum of **2** recorded in $CDCl_3$



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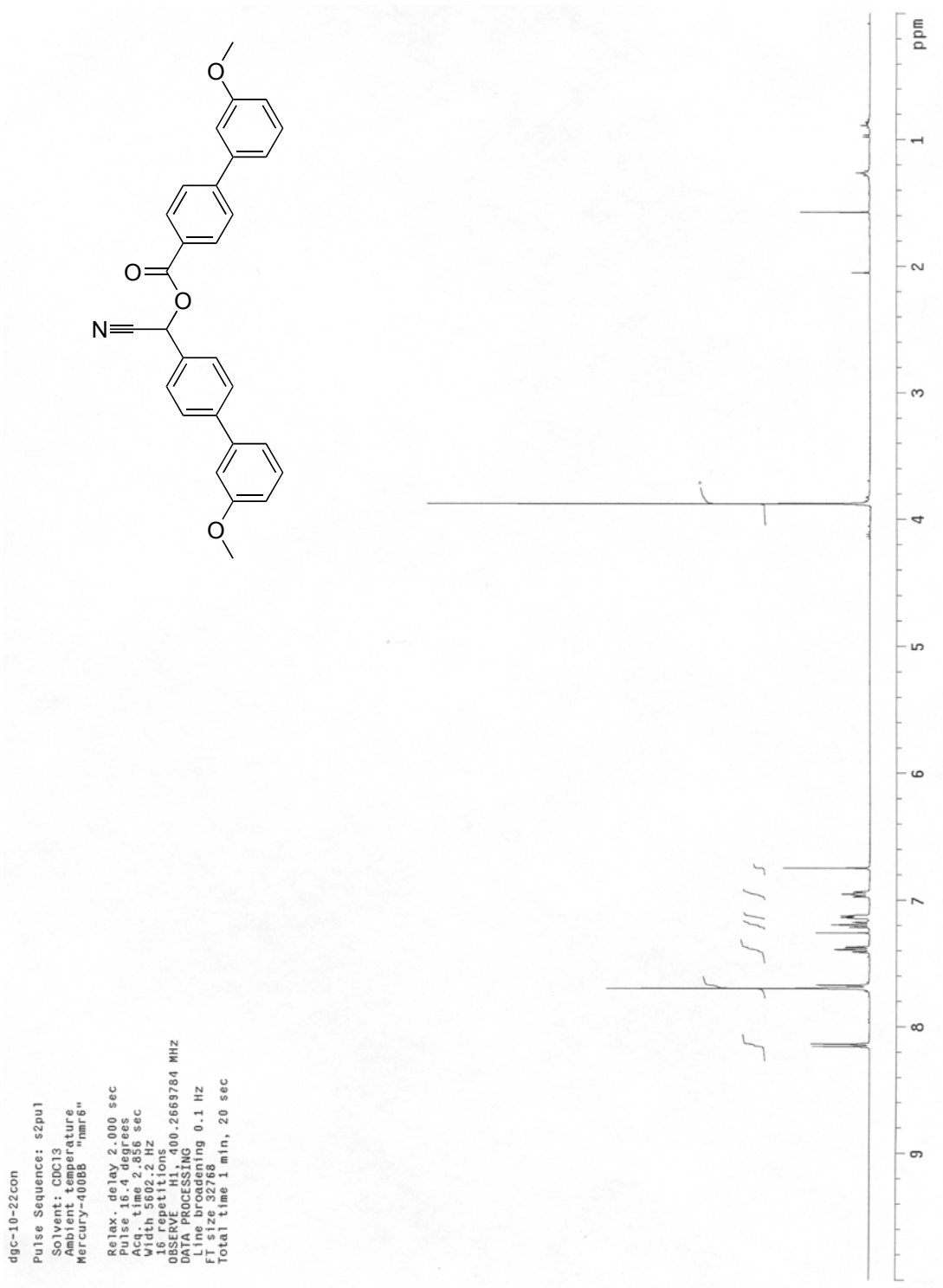

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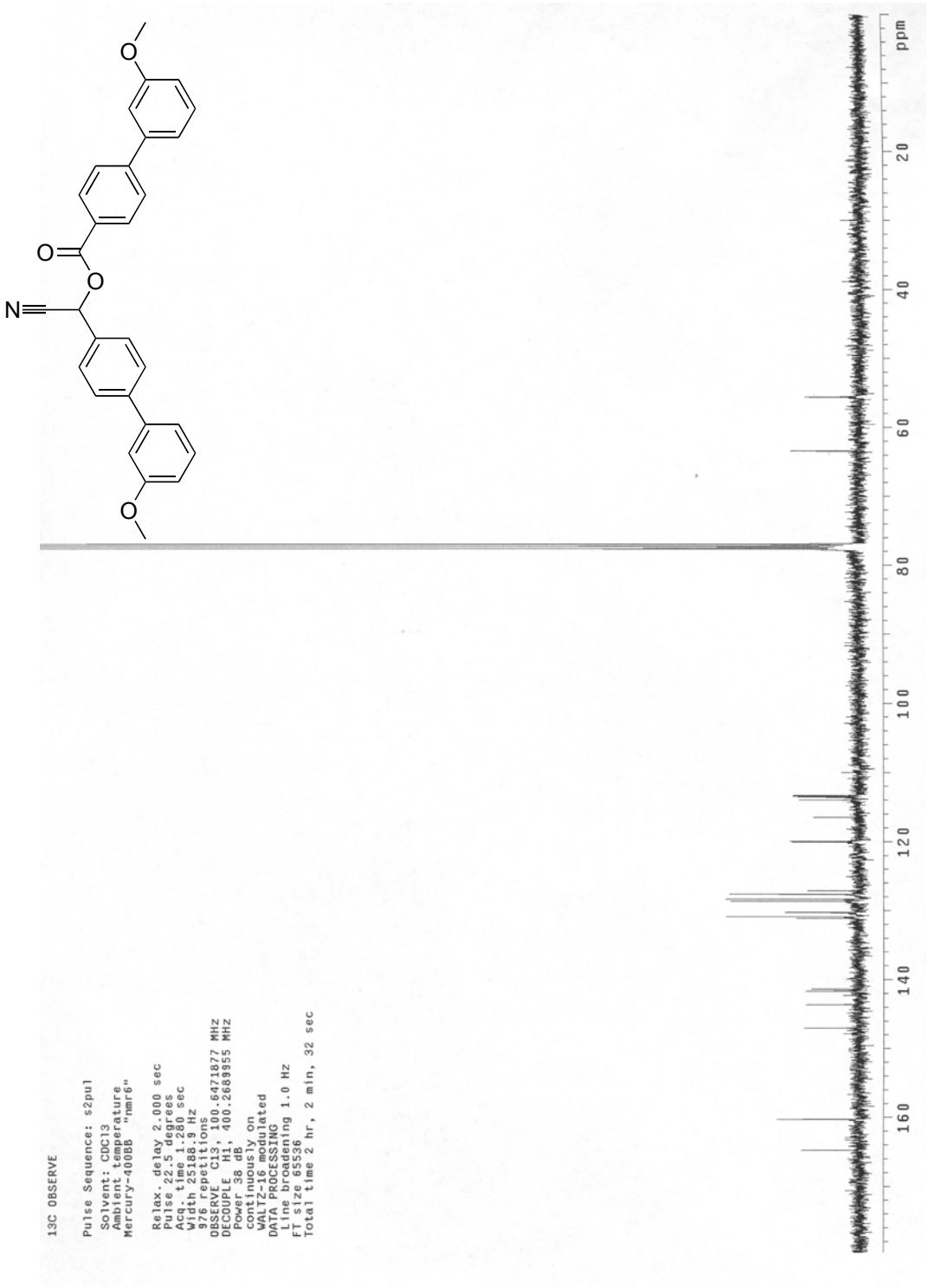

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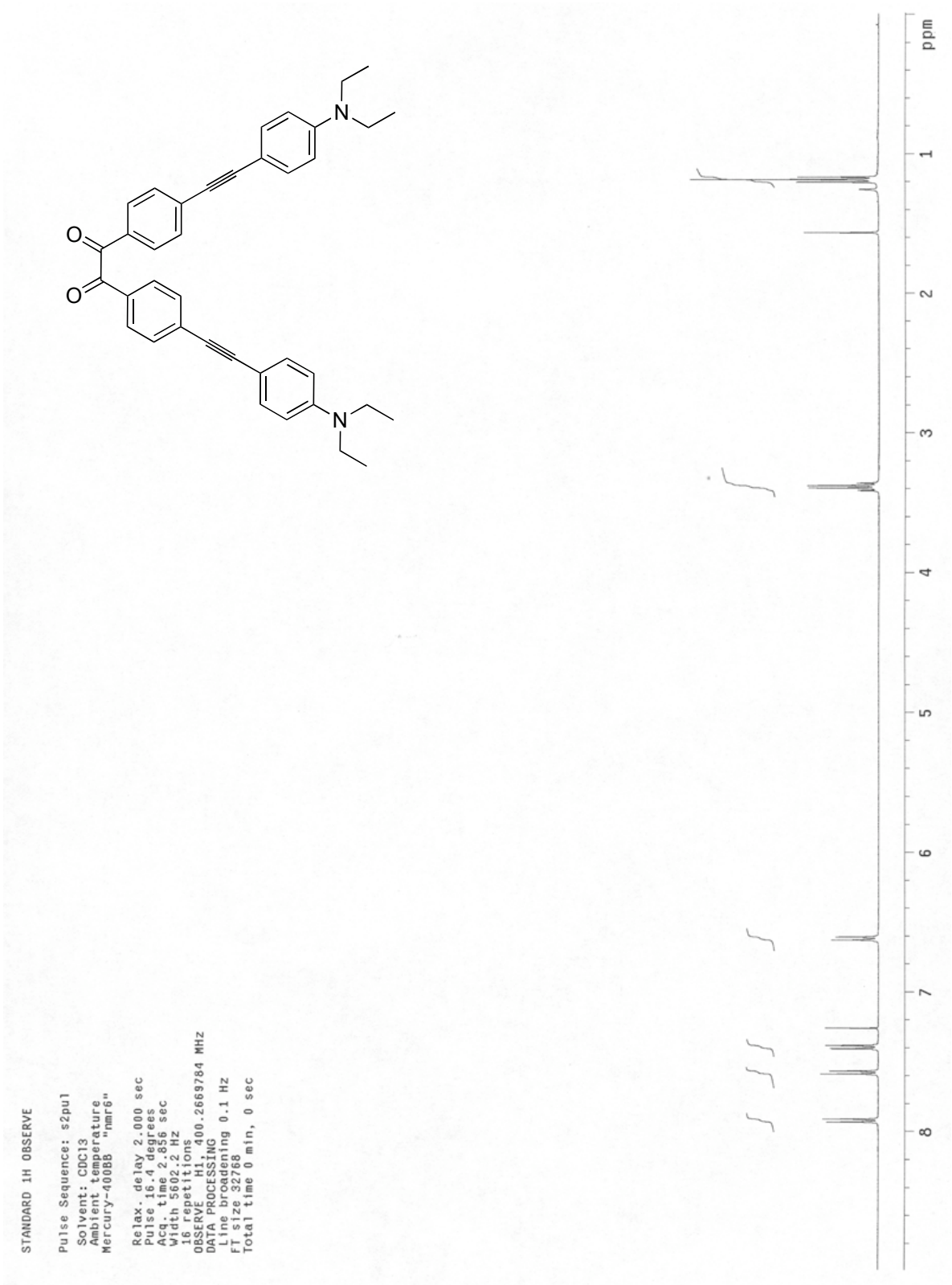

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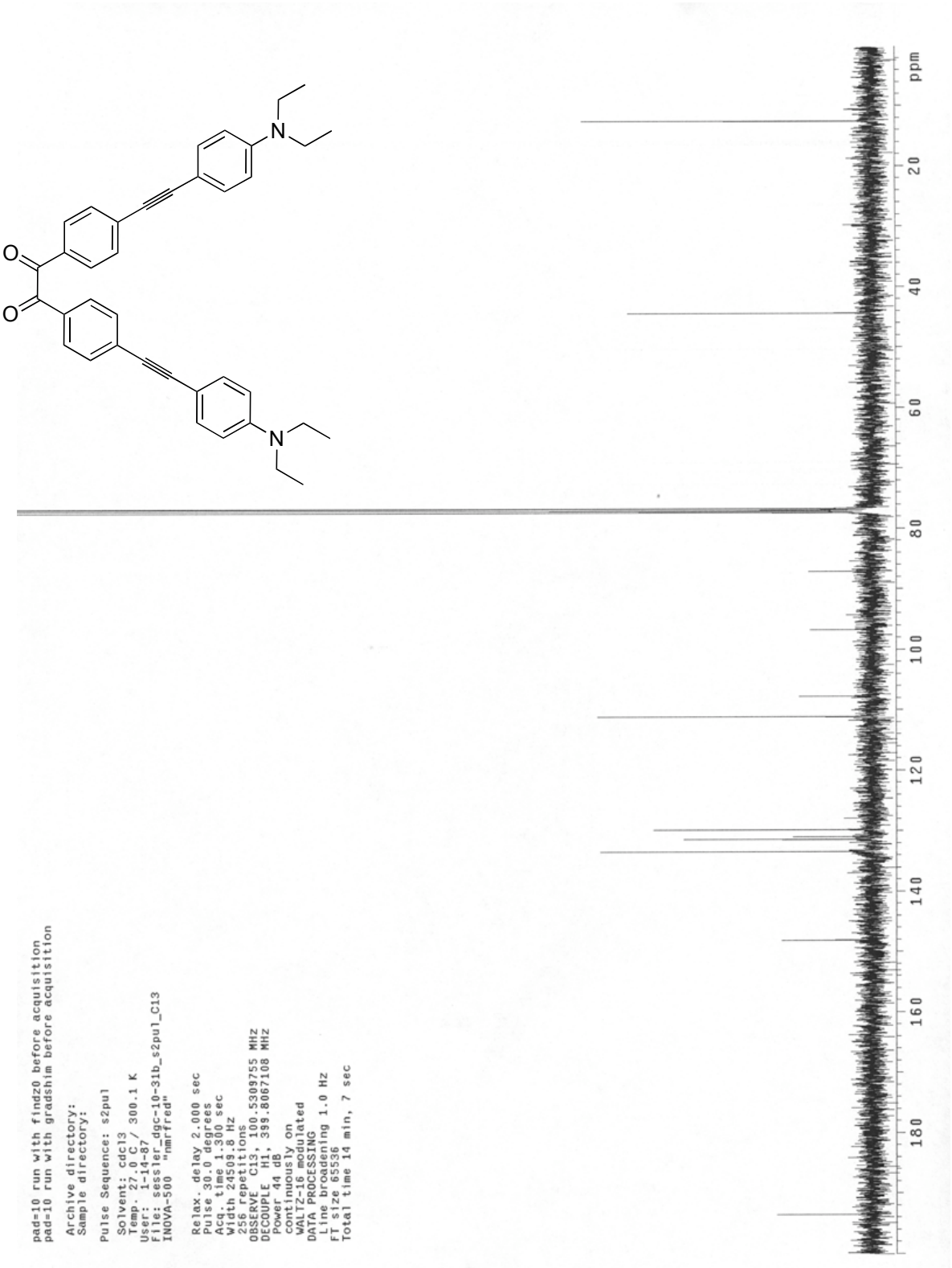

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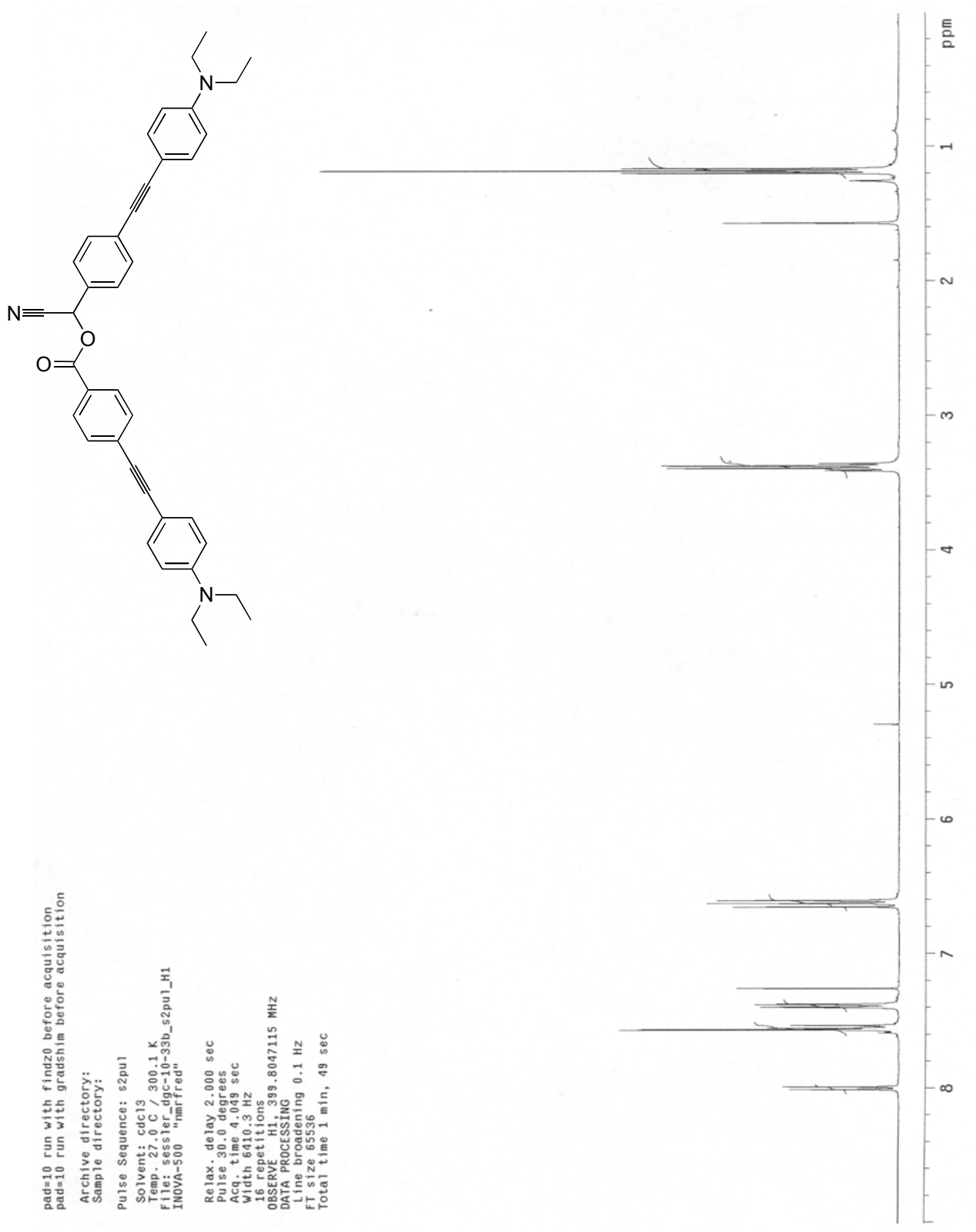
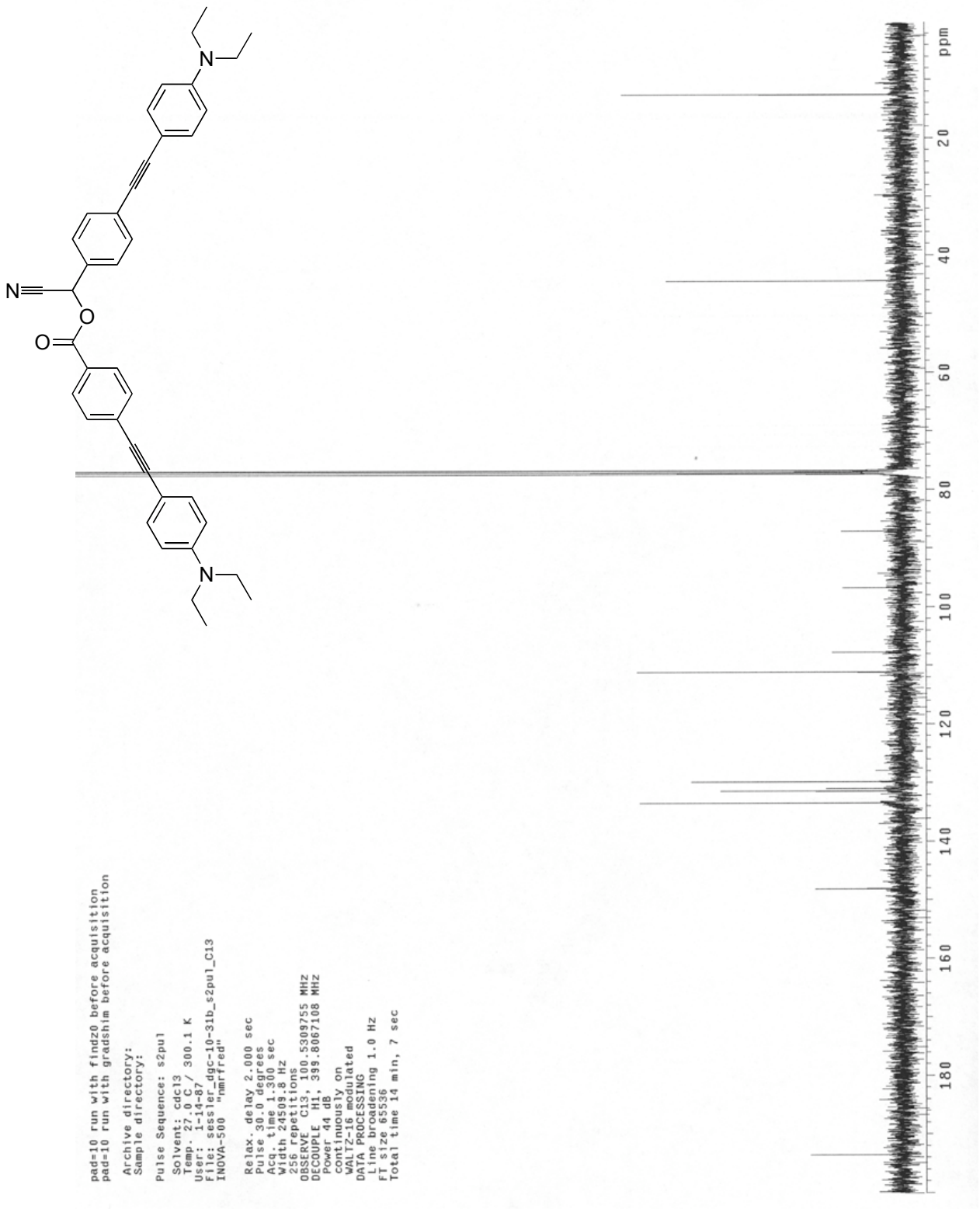


^{1}H NMR spectrum of **3a** recorded in $CDCl_3$



^{13}C NMR spectrum of **3a** recorded in $CDCl_3$

Shimadzu HPLC Testing - Sessler Lat
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Batch Filename	:
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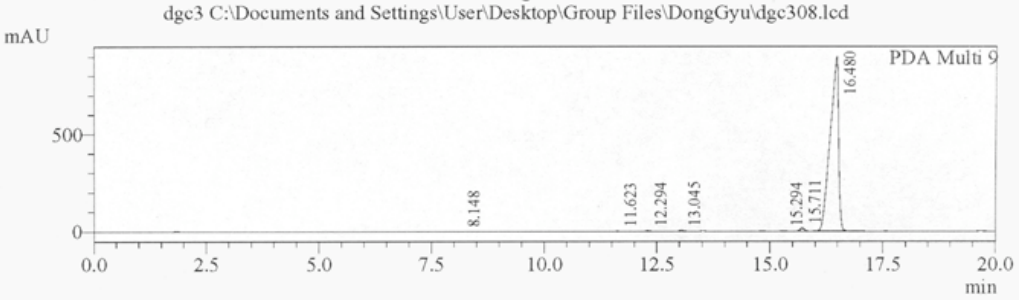

1 PDA Multi 9 / 380nm 4nm

PeakTable

PDA Ch9 380nm 4nm

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3	12.294	23449	0.198
4	13.045	32495	0.274
5	15.294	17886	0.151
6	15.711	101298	0.854
7	16.480	11663956	98.387
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Method

<<Comment>>
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17.99	Pumps	B.Conc	99
18.00	Pumps	B.Conc	10
25.00	Controller	Stop	

A: 0.1 % TFA in Water
B: Acetonitrile

HPLC analysis of **3**

Shimadzu HPLC Testing - Sessler Lat
\Documents and Settings\User\Desktop\Group Files\DongGyu\dgc3a2.lcd dgc3a2

Sample Information

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Sample ID	: dgc3a
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Vail#	: 42
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Method Filename	: ACN 20 pct 1 ml min Base Method no frc 081107.lcm
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Chromatogram

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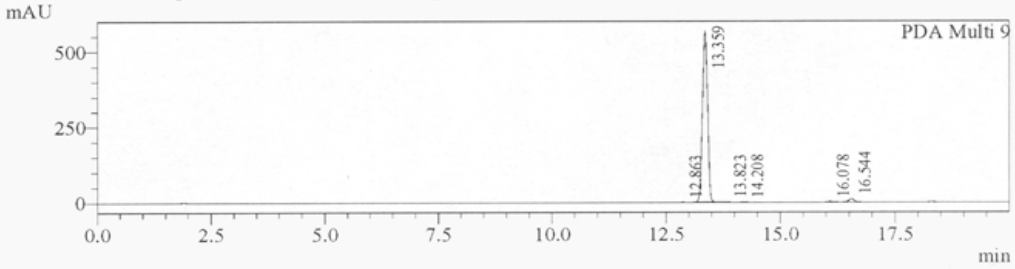

1 PDA Multi 9 / 380nm 4nm

PeakTable

PDA Ch9 380nm 4nm

Peak#	Ret. Time	Area	Area %
1	12.863	3491	0.077
2	13.359	4381905	97.219
3	13.823	6145	0.136
4	14.208	7101	0.158
5	16.078	17344	0.385
6	16.544	91245	2.024
Total		4507230	100.000

Method

<<Comment>>
<<LC Program>>

Time	Unit	Command	Value
2.00	Pumps	B.Conc	20
5.00	Pumps	B.Conc	70
7.00	Pumps	B.Conc	70
10.00	Pumps	B.Conc	90
17.99	Pumps	B.Conc	99
18.00	Pumps	B.Conc	10
25.00	Controller	Stop	

A: 0.1 % TFA in Water
B: Acetonitrile

HPLC analysis of **3a**