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Supporting Information

[Fe(F$_{20}$TPP)Cl]-Catalyzed Amination with Arylamines and {[Fe(F$_{20}$TPP)(NAr)](PhI=NAr)}$^{+\cdot}$ Intermediate Assessed by High-Resolution ESI-MS and DFT Calculations

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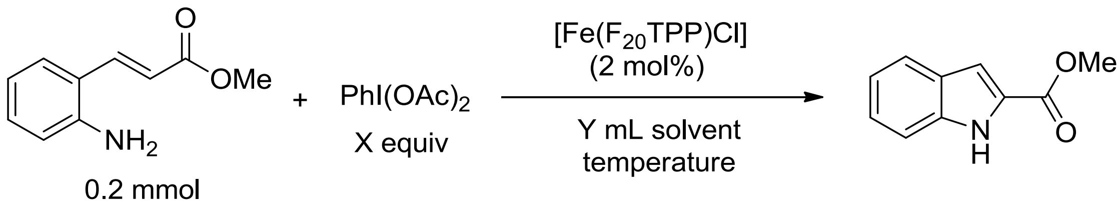
General: Analytical grade chemicals (purchased from Sigma-Aldrich Chemical Co.) and analytical grade organic solvents were used throughout the experiments, unless otherwise specified. All manipulations were carried out using standard Schlenk line under an atmosphere of argon. Solvents were pre-dried over activated 4 Å molecular sieves and refluxed over sodium (toluene) or calcium hydride (1,2-dichloroethane and acetonitrile) under an argon atmosphere and collected by distillation. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX-300, AV-400, or DRX-500 NMR spectrometer. ^{1}H and ^{13}C NMR spectra were referenced internally to residual protio-solvent (^{1}H) or solvent (^{13}C) resonances and are reported relative to tetramethylsilane. The following abbreviations are used to indicate the multiplicity in NMR spectra: s – singlet; d – doublet; t – triplet; q – quartet; quint. – quintet; dd – double doublet; dt – double triplet; m – multiplet; brs – broad signal. EI mass spectra (including HRMS) were measured on a Finnigan MAT 95 mass spectrometer (Thermo Electron, San Jose, US). Positive-ion ESI mass spectra were obtained on a Waters Micromass Q-TOF Premier quadrupole-time of flight tandem mass spectrometer (Waters Corporation, Milford, USA).

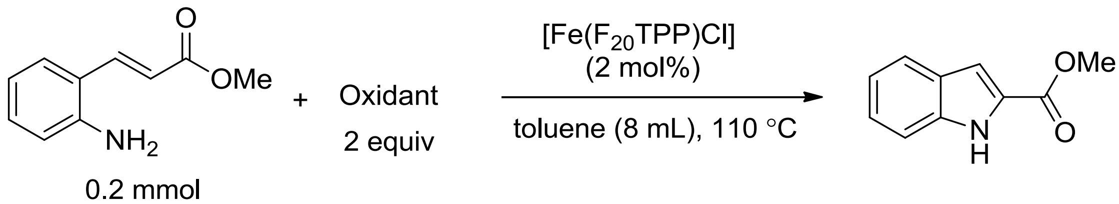
Table S1. Optimization of reaction conditions by using the synthesis of methyl indole-2-carboxylate as a model reaction



Entry	X	Y	Solvent	T [℃].	t [h]	Conversion [%]	Yield [%]
1	1.5	8	DCE	80	3	100%	29%
2[a]	1.5	8	DCE	80	3	100%	29%
3[b]	1.5	8	DCE	80	3	72%	17%
4	1.5	8	MeCN	80	3	58%	17%
5	1.5	8	Toluene	110	3	86%	46%
6	1.5	2	Toluene	110	3	90%	7%
7[c]	1.5	8	Toluene	rt	12	85%	34%
8[c]	1.5	8	Toluene	110	3	78%	40%
9[d]	2.0	8	Toluene	110	3	100%	65%
10[e]	2.0	8	Toluene	110	3	100%	68%

Reaction conditions: [a] $PhI(OAc)_2$ added in three portions (0.5 equiv / 0.5 h). [b] Substrate and $PhI(OAc)_2$ were added simultaneously by syringe pump in 3 h. [c] 1.5 equiv of K_2CO_3 was added. [d] $PhI(OAc)_2$ was added in two portions (1.0 equiv / 0.5 h). [e] 4 Å MS (120 mg) was added and $PhI(OAc)_2$ was added in five portions (0.08 mmol / 0.5 h). DCE: 1,2-dichloroethane.

Table S2. Test of different oxidants using the synthesis of methyl indole-2-carboxylate as a model reaction



Entry	Oxidant	Time [h]	Conversion [%]	Yield [%]
1	$PhI(OAc)_2$	3	100	65
2	30% H_2O_2	3	20	<5
3	$NaIO_4$	3	<5	/
4	DDQ	3	100	/

The reactions were performed with 0.20 mmol substrate and 0.004 mmol [Fe(F_{20}TPP)Cl] (2 mol %) in 8 mL of anhydrous toluene under N_2. The mixture was heated to reflux and then 0.4 mmol of oxidant was added in five portions (0.08 mmol / 0.5 h).

General procedure for [Fe(F_{20}TPP)Cl]-catalyzed intramolecular amination of sp^2 C–H bonds (Table 1)

A. Synthesis of indoles

To a mixture of substrate (0.20 mmol), [Fe(F_{20}TPP)Cl] (0.004 mmol, 2 mol%), and 4 Å molecular sieves (120 mg) in refluxing anhydrous toluene (8 mL) under N_2, $PhI(OAc)_2$ (0.4 mmol, 129 mg) was added in five portions (0.08 mmol / 0.5 h). The reactions were monitored by thin layer chromatography (TLC) and completed within 3 h. After removing toluene in reduced pressure, the residue was purified by flash column chromatography to give the desired product.

B. Synthesis of phenyl benzimidazoles

A mixture of phenylenediamine (0.2 mmol), benzaldehyde (0.2 mmol), [Fe(F_{20}TPP)Cl] (0.004 mmol, 2 mol%), and 4 Å molecular sieves (180 mg) in anhydrous toluene (8 mL) under N_2 was stirred at room temperature for 3 h. Then the mixture was heated to reflux and $PhI(OAc)_2$ (0.4 mmol, 129 mg) was added in five portions (0.08 mmol / 0.5 h) and the reactions were further stirred for an hour. After removing toluene in reduced pressure, the residue was purified by flash column chromatography to give the desired product.

General procedure for [Fe(F_{20}TPP)Cl]-catalyzed intramolecular amination of sp^3 C–H bonds (Table 2)

To a mixture of substrate (0.20 mmol), [Fe(F_{20}TPP)Cl] (0.004 mmol, 2 mol%), and 4 Å molecular sieves (120 mg) in refluxing anhydrous toluene (8 mL) under N_2, PhI(OAc)$_2$ (0.4 mmol, 129 mg) was added in five portions (0.08 mmol / 0.5 h). The reactions were monitored by thin layer chromatography (TLC) and completed within 3 h. After removing toluene in reduced pressure, the residue was purified by flash column chromatography to give the desired product.

General procedure for [Fe(F_{20}TPP)Cl]-catalyzed intermolecular amination reactions (Table 3)

To a mixture of substrate (10 mmol), [Fe(F_{20}TPP)Cl] (0.004 mmol, 2 mol%), and 4 Å molecular sieves (120 mg) in toluene (1.5 mL) at 120 °C, nitrogen source (0.2 mmol) and PhI(OAc)$_2$ (0.4 mmol, 129 mg) were jointly added in five portions (0.004 mmol / 0.5 h and 0.08 mmol / 0.5 h, respectively). The reactions were monitored by thin layer chromatography (TLC) and completed within 3 h. After removing toluene in reduced pressure, the residue was purified by flash column chromatography to give the desired product. For tetralin and indan, the reactions were performed with 10 mmol of substrate without toluene under similar conditions.

ESI-MS experiments

Positive-ion ESI mass spectra were obtained on a Waters Micromass Q-Tof Premier quadrupole time-of-flight tandem mass spectrometer. For the detection of *m/z* 1504.1 ion, an acetonitrile solution of [Fe(F_{20}TPP)Cl] (1 mM) was treated with 10 equiv of *p*-nitroaniline and PhI(OAc)$_2$ (both were 20 mM solutions in MeCN). The final concentration of iron in the reaction mixture was 0.5 mM. After heating at ca. 60 °C for 30 s, the mixture was introduced into the ESI source by using a syringe pump (flow rate: 5 μL min^{-1}). The mass resolution was fixed at about 8000 (full width at half-height).

DFT calculations

Optimization of the geometry of the proposed intermediate $\{[Fe(F_{20}TPP)(NC_6H_4\text{-}p\text{-}NO_2)](PhI{=}NC_6H_4\text{-}p\text{-}NO_2)\}^{+\cdot}$ (complex **A**) was carried out with the density functional M06L and double-zeta quality basis set (6-31G* for C, H, N, F atoms, SDD for Fe atom, and SDD conjunction with a 0.266 d polarization for I atom) through Gaussian09 programm.[1]

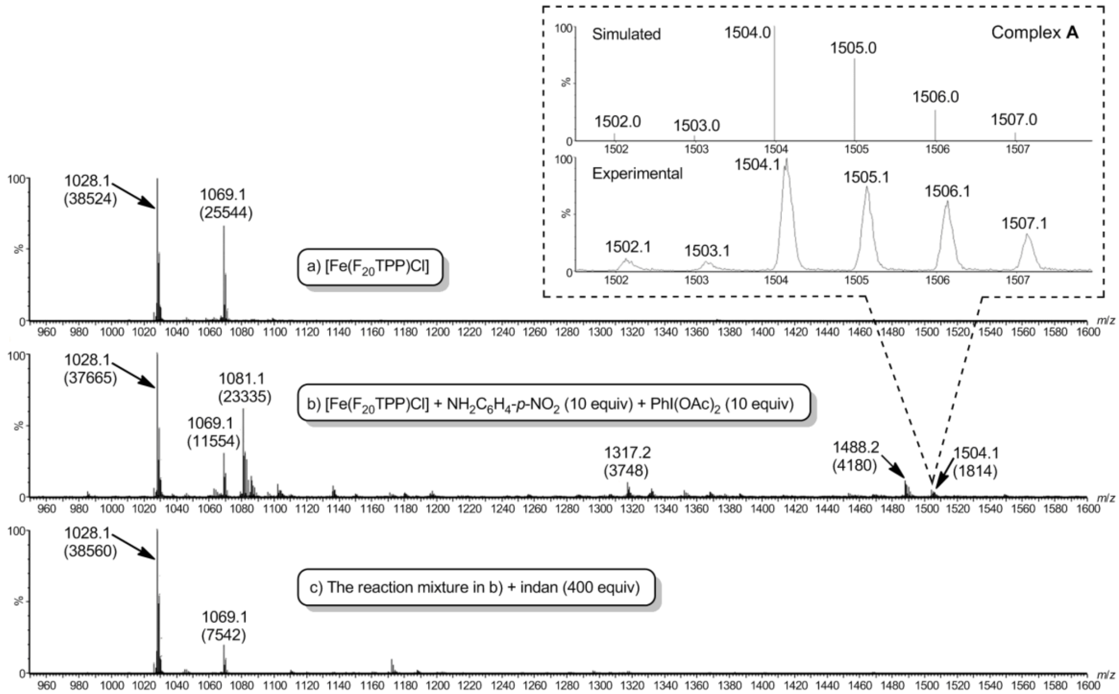
The free energy difference (ΔG) between the complex **A** and the separated $[Fe(F_{20}TPP)(NC_6H_4\text{-}p\text{-}NO_2)]$ unit and $[PhI{=}NC_6H_4\text{-}p\text{-}NO_2]^{+\cdot}$ unit was calculated based on the geometries optimized by M06L/6-31G* (SDD), B3LYP-D3 [2] together with triplet-zeta quality basis set (6-311G* (SDD)) used for single point energy correction. The solvation energies were computed using the PCM solvation model, employing acetonitrile as the solvent.

References

[1] Gaussian 09, Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian, Inc., Wallingford, CT, **2011**.

[2] a) S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.* **2010**, *132*, 154104; b) S. Grimme, *J. Comput. Chem.* **2006**, *27*, 1787–1799.

Peak assignments of Figure 2



All detected signals are mono-cationic:

m/z	Proposed composition
1028.1	$Fe(F_{20}TPP)$
1069.1	$Fe(F_{20}TPP)$ + MeCN
1081.1	$Fe(F_{20}TPP)$ + H_2O + Cl
1317.2	$Fe(F_{20}TPP)$ + NHAr + O=NAr
1488.2	$Fe(F_{20}TPP)$ + H_2NAr + $PhI(OAc)_2$
1504.1	**$Fe(F_{20}TPP)$ + NAr + PhI=NAr**

Ar = C_6H_4-*p*-NO_2

Cartesian coordinates

$[Fe(F_{20}TPP)(NC_6H_4\text{-}p\text{-}NO_2)(PhI{=}NC_6H_4\text{-}p\text{-}NO_2)]^{+\cdot}$ (S = 1/2, ααβ)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.450199	-1.472508	1.419390
2	6	0	2.068923	-1.519462	1.061126
3	6	0	3.830243	-0.172564	1.346923
4	1	0	4.063954	-2.334829	1.650138
5	7	0	1.590272	-0.252779	0.796376
6	6	0	1.361358	-2.705505	0.888903
7	6	0	2.670580	0.584092	0.979206
8	1	0	4.821378	0.235693	1.499320
9	6	0	2.057375	-3.979585	1.192996
10	6	0	0.047249	-2.753340	0.437732
11	6	0	2.673239	1.968026	0.791990
12	6	0	2.464733	-4.862083	0.191990
13	6	0	2.343815	-4.334781	2.513017
14	7	0	-0.769349	-1.657595	0.214769
15	6	0	-0.657885	-3.965149	0.162189
16	6	0	1.543739	2.690536	0.413503
17	6	0	3.950222	2.688804	0.993755
18	6	0	3.121927	-6.051843	0.480938

19	9	0	2.232280	-4.564169	-1.096236
20	6	0	3.000954	-5.518454	2.828857
21	9	0	1.984572	-3.520774	3.508012
22	6	0	-1.991954	-2.191249	-0.147318
23	6	0	-1.914804	-3.616758	-0.212966
24	1	0	-0.236889	-4.959989	0.239798
25	7	0	0.296330	2.161445	0.157934
26	6	0	1.519313	4.117999	0.301293
27	6	0	4.577303	3.365907	-0.055387
28	6	0	4.624214	2.665991	2.218255
29	6	0	3.389466	-6.380514	1.807284
30	9	0	3.497342	-6.869609	-0.498600
31	9	0	3.253499	-5.832343	4.093011
32	6	0	-3.165332	-1.467106	-0.349771
33	1	0	-2.727271	-4.268429	-0.511024
34	6	0	-0.513860	3.254235	-0.062889
35	6	0	0.243625	4.467751	0.005633
36	1	0	2.369639	4.769864	0.457646
37	6	0	5.838520	3.930385	0.073783
38	9	0	3.970910	3.454320	-1.252394
39	6	0	5.879054	3.242587	2.380853
40	9	0	4.066175	2.061961	3.271389
41	9	0	4.012409	-7.512991	2.097863
42	6	0	-4.422470	-2.205291	-0.603663
43	6	0	-3.214199	-0.075002	-0.320854

44	6	0	-1.894477	3.217244	-0.254179
45	1	0	-0.159575	5.463202	-0.131507
46	6	0	6.495957	3.864067	1.298269
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48	9	0	6.489334	3.200059	3.559358
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53	6	0	-2.635628	2.040101	-0.281726
54	6	0	-2.604525	4.502238	-0.459660
55	9	0	7.698185	4.396964	1.431716
56	6	0	-6.328330	-2.705648	-2.044500
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61	1	0	-5.410246	0.273127	-0.552967
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63	6	0	-2.368405	5.267369	-1.603702
64	6	0	-6.838754	-3.577056	-1.086353
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66	9	0	-6.644850	-4.591955	1.029304
67	1	0	-4.697202	2.863365	-0.543396
68	6	0	-4.179469	6.211429	0.268405

69	9	0	-3.784801	4.308929	1.581314
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71	9	0	-1.499189	4.831833	-2.523040
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76	9	0	-4.541615	8.103853	-1.081841
77	26	0	-0.338138	0.261992	0.558517
78	7	0	-0.830551	0.514925	2.167333
79	6	0	-2.037849	0.462903	2.766320
80	6	0	-2.806070	-0.730106	2.859499
81	6	0	-2.548989	1.665358	3.329244
82	6	0	-4.047647	-0.707456	3.462650
83	1	0	-2.399100	-1.654573	2.456441
84	6	0	-3.802042	1.683697	3.906497
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90	8	0	-6.257936	1.588808	5.038521
91	8	0	-6.518693	-0.523711	4.540185
92	1	0	-3.422039	-2.874445	-4.040669
93	6	0	-2.355491	-2.965084	-3.851447

94	6	0	-1.637826	-1.823700	-3.490469
95	6	0	-1.714769	-4.195757	-3.970576
96	6	0	-0.275043	-1.977678	-3.283182
97	1	0	-2.144052	-0.867532	-3.374247
98	6	0	-0.347417	-4.302790	-3.733195
99	1	0	-2.285886	-5.076471	-4.254709
100	53	0	0.875585	-0.216493	-2.784947
101	6	0	0.404960	-3.176703	-3.397831
102	1	0	0.157548	-5.262528	-3.822206
103	7	0	2.448515	-1.462036	-2.127271
104	1	0	1.473640	-3.240116	-3.219197
105	6	0	3.653104	-0.889365	-1.990197
106	6	0	4.671022	-1.832714	-1.608513
107	6	0	4.038742	0.471385	-2.149732
108	6	0	5.958138	-1.416110	-1.366165
109	1	0	4.384113	-2.877186	-1.507915
110	6	0	5.333441	0.874932	-1.912798
111	1	0	3.299254	1.208057	-2.467057
112	6	0	6.280456	-0.059980	-1.493565
113	1	0	6.730816	-2.118871	-1.066674
114	1	0	5.636729	1.907513	-2.050293
115	7	0	7.615874	0.401192	-1.146885
116	8	0	7.785194	1.621055	-1.059366
117	8	0	8.474790	-0.454432	-0.942880

[Fe(F_{20}TPP)(NC_6H_4-*p*-NO_2)(PhI=NC_6H_4-*p*-NO_2)]$^{+\cdot}$ (*S* = 3/2, ααα)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.437799	-1.533442	1.364461
2	6	0	2.059507	-1.563350	1.001777
3	7	0	1.588001	-0.285499	0.766578
4	6	0	2.664137	0.542062	0.983424
5	6	0	3.824094	-0.230582	1.329434
6	6	0	1.333863	-2.746235	0.837743
7	6	0	2.027352	-4.025878	1.127949
8	6	0	2.419345	-4.905247	0.118603
9	6	0	3.066593	-6.103577	0.394108
10	6	0	3.340390	-6.443788	1.716212
11	6	0	2.967507	-5.585000	2.746379
12	6	0	2.319460	-4.392797	2.443519
13	9	0	2.179484	-4.595171	-1.166060
14	9	0	3.427431	-6.918289	-0.594142
15	9	0	3.226123	-5.910673	4.006281
16	9	0	1.975825	-3.582437	3.446211
17	26	0	-0.334614	0.246894	0.502544
18	7	0	-0.802573	-1.689560	0.218113

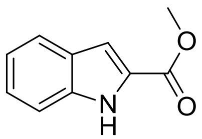
19	6	0	-2.031766	-2.209574	-0.108895
20	6	0	-1.979417	-3.642258	-0.156217
21	6	0	-0.718501	-4.001603	0.186670
22	6	0	0.007435	-2.788711	0.429982
23	6	0	-3.191497	-1.462987	-0.335950
24	6	0	-4.462109	-2.186809	-0.566206
25	6	0	-5.175485	-2.045163	-1.759376
26	6	0	-6.379093	-2.697182	-1.990470
27	6	0	-6.906616	-3.525487	-1.003781
28	6	0	-6.224237	-3.693254	0.197772
29	6	0	-5.019749	-3.029015	0.401744
30	9	0	-4.689922	-1.266940	-2.743051
31	9	0	-7.018170	-2.541619	-3.145366
32	9	0	-6.727883	-4.478988	1.140766
33	9	0	-4.392685	-3.212289	1.569939
34	6	0	2.663989	1.935247	0.858873
35	6	0	1.538590	2.675515	0.501730
36	7	0	0.296387	2.157019	0.210854
37	6	0	-0.500559	3.254240	-0.024987
38	6	0	0.256464	4.467585	0.093008
39	6	0	1.520037	4.108699	0.422640
40	6	0	-1.869377	3.217352	-0.283945
41	6	0	-2.611450	2.039280	-0.354129
42	7	0	-2.108846	0.756531	-0.252288
43	6	0	-3.212992	-0.070535	-0.366722

44	6	0	-4.403113	0.705172	-0.545014
45	6	0	-4.029200	2.008209	-0.554087
46	6	0	3.941326	2.647109	1.094699
47	6	0	4.575912	3.362888	0.076437
48	6	0	5.828913	3.937974	0.239047
49	6	0	6.473379	3.835747	1.468048
50	6	0	5.852339	3.166730	2.519587
51	6	0	4.603601	2.586247	2.324305
52	9	0	3.985631	3.484278	-1.126994
53	9	0	4.042089	1.938813	3.348431
54	9	0	6.453070	3.084751	3.700734
55	9	0	6.413382	4.562565	-0.776369
56	6	0	-2.568503	4.506011	-0.508423
57	6	0	-3.512193	5.008039	0.389548
58	6	0	-4.158407	6.220110	0.175464
59	6	0	-3.857393	6.964532	-0.961988
60	6	0	-2.916949	6.493782	-1.874181
61	6	0	-2.289093	5.277166	-1.638746
62	9	0	-3.815691	4.312608	1.492477
63	9	0	-5.051170	6.671383	1.048859
64	9	0	-2.630855	7.203029	-2.960995
65	9	0	-1.387984	4.843716	-2.528622
66	1	0	-2.807692	-4.286090	-0.426915
67	1	0	-0.305649	-4.999969	0.266562
68	1	0	4.045863	-2.402717	1.584287

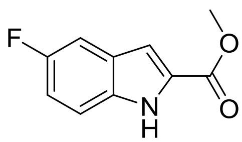
69	1	0	4.814807	0.170487	1.505731
70	1	0	2.366377	4.755159	0.618931
71	1	0	-0.140976	5.466080	-0.040399
72	1	0	-4.659985	2.879225	-0.680764
73	1	0	-5.402097	0.300066	-0.646908
74	9	0	3.954895	-7.584059	1.994820
75	9	0	7.666613	4.380065	1.637012
76	9	0	-4.466694	8.120958	-1.176299
77	9	0	-8.051440	-4.157243	-1.209737
78	7	0	2.515859	-1.425610	-2.069751
79	6	0	3.713789	-0.840089	-1.941560
80	6	0	4.748316	-1.781415	-1.599562
81	6	0	4.078151	0.531096	-2.076701
82	6	0	6.043328	-1.360844	-1.406628
83	1	0	4.473229	-2.829305	-1.506262
84	6	0	5.378767	0.939246	-1.885733
85	1	0	3.317813	1.270235	-2.331943
86	6	0	6.347723	-0.002182	-1.533631
87	1	0	6.833340	-2.061538	-1.151309
88	1	0	5.668500	1.978445	-2.002204
89	7	0	7.704548	0.460696	-1.247804
90	8	0	7.869823	1.677402	-1.150693
91	8	0	8.570988	-0.397181	-1.104475
92	7	0	-0.844669	0.426037	2.159512
93	6	0	-2.077665	0.452631	2.712942

94	6	0	-2.813412	-0.740647	2.945591
95	6	0	-2.650555	1.697177	3.091701
96	6	0	-4.075482	-0.686672	3.504114
97	1	0	-2.368186	-1.694229	2.668826
98	6	0	-3.908379	1.746222	3.659793
99	1	0	-2.083469	2.608359	2.912499
100	6	0	-4.607949	0.555049	3.850243
101	1	0	-4.662287	-1.583569	3.677851
102	1	0	-4.370453	2.685661	3.949315
103	7	0	-5.956870	0.610256	4.424832
104	8	0	-6.377391	1.711874	4.769696
105	8	0	-6.573970	-0.449523	4.513313
106	53	0	0.919852	-0.206321	-2.708054
107	6	0	-0.207218	-1.975278	-3.233831
108	6	0	-1.578419	-1.837947	-3.390000
109	6	0	0.493378	-3.153756	-3.415929
110	6	0	-2.285761	-2.980795	-3.767458
111	1	0	-2.098185	-0.897164	-3.219668
112	6	0	-0.250319	-4.282990	-3.759823
113	1	0	1.568666	-3.205076	-3.280071
114	6	0	-1.626970	-4.193960	-3.946276
115	1	0	-3.359245	-2.904519	-3.918100
116	1	0	0.268029	-5.229549	-3.898689
117	1	0	-2.191417	-5.076405	-4.237920

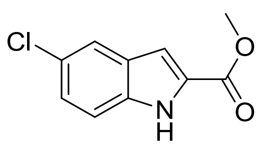
Characterization of amination products

 *J. Med. Chem.* **2004**, *47*, 5298–5310.

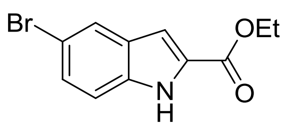
^{1}H NMR (300 MHz, $CDCl_3$), δ 8.91 (brs, 1H), 7.70 (d, *J* = 7.8 Hz, 1H), 7.43 (dd, *J* = 8.4, 0.6 Hz, 1H), 7.33 (td, *J* = 7.8, 1.2 Hz, 1H), 7.28 (d, J=0.6 Hz, 1H), 7.16 (td, J=7.8, 0.6 Hz, 1H), 3.95 (s, 3H).

 *Org. Lett.* **2008**, *10*, 4899–4901.

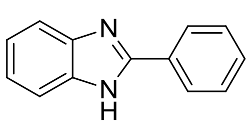
^{1}H NMR (300 MHz, $CDCl_3$), δ 8.90 (brs, 1H), 7.35 (dd, *J* = 9.0, 3.9 Hz, 1H), 7.31-7.26 (m, 1H), 7.17 (s, 1H), 7.09 (td, *J* = 9.3, 1.5 Hz, 1H), 3.95 (s, 3H).

 *Org. Lett.* **2008**, *10*, 4899–4901.

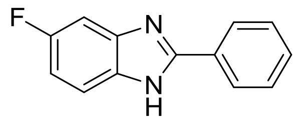
^{1}H NMR (300 MHz, $CDCl_3$), δ 8.99 (brs, 1H), 7.66 (s, 1H), 7.35 (d, *J* = 8.4 Hz, 1H), 7.28 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.15 (d, *J* = 0.9 Hz, 1H), 3.95 (s, 3H).

 *Synth. Commun.* **2009**, *39*, 2506–2515.

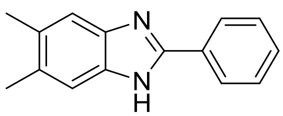
^{1}H NMR (400 MHz, $CDCl_3$), δ 9.03 (brs, 1H), 7.83 (d, *J* = 2.0 Hz, 1H), 7.40 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.30 (d, *J* = 9.2 Hz, 1H), 7.15 (d, *J* = 2.0 Hz, 1H), 4.42 (q, *J* = 7.2 Hz, 2H), 1.42 (t, *J* = 7.2 Hz, 3H).

 *Chem. Asian J.* **2009**, *4*, 1551–1561.

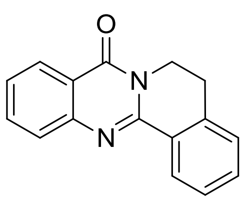
^{1}H NMR (400 MHz, DMSO-d_6), δ 8.27-8.25 (m, 2H), 7.74-7.70 (m, 2H), 7.68-7.61 (m, 3H), 7.40-7.35 (m, 2H).


Org. Lett. **2008**, *10*, 3367–3370.

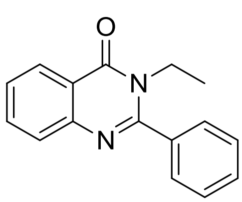
^{1}H NMR (400 MHz, DMSO-d_6), δ 8.17-8.14 (m, 2H), 7.61-7.48 (m, 4H), 7.39 (d, *J* = 9.2 Hz, 1H), 7.09-7.04 (m, 1H).


Org. Lett. **2008**, *10*, 3367–3370.

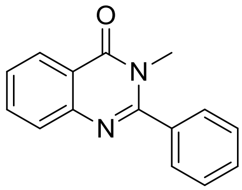
^{1}H NMR (400 MHz, DMSO-d_6), δ 12.63 (brs, 1H), 8.12 (d, *J* = 7.6 Hz, 2H), 7.52 (t, *J* = 7.6 Hz, 2H), 7.47-7.25 (m, 3H), 2.32 (s, 6H).


Org. Biomol. Chem. **2007**, *5*, 103–113.

^{1}H NMR (400 MHz, $CDCl_3$), δ 8.50 (d, *J* = 8.0 Hz, 1H), 8.32 (d, *J* = 8.0 Hz, 1H), 7.79-7.4 (m, 2H), 7.51-7.43 (m, 3H), 7.32 (d, *J* = 8.0 Hz, 1H), 4.43 (t, *J* = 6.4 Hz, 2H), 3.11 (t, *J* = 6.4 Hz, 2H).

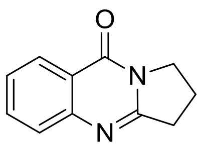

Chin. Pharm. J. **2000**, *52*, 167–177.

^{1}H NMR (300 MHz, $CDCl_3$), δ 8.34 (d, *J* = 7.8 Hz, 1H), 7.79-7.72 (m, 2H), 7.56-7.48 (m, 6H), 4.04 (q, *J* = 6.9 Hz, 2H), 1.22 (t, *J* = 6.9 Hz, 3H).



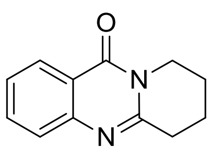
Chin. Pharm. J. **2000**, *52*, 167–177.

[1]H NMR (400 MHz, $CDCl_3$), δ 8.34 (d, *J* = 8.0 Hz, 1H), 7.79-7.74 (m, 2H), 7.58-7.50 (m, 6H), 3.50 (s, 3H).



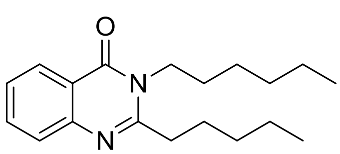
J. Am. Chem. Soc. **2008**, *130*, 416–417.

[1]H NMR (400 MHz, $CDCl_3$), δ 8.28 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.73 (td, *J* =7.6, 2.0 Hz, 1H), 7.65 (d, *J* =7.2 Hz, 1H), 7.45 (td, *J* = 7.8, 1.2Hz, 1H), 4.21 (t, *J* = 7.2 Hz, 2H), 3.18 (t, *J* = 8.0 Hz, 2H), 2.33-2.26 (m, 2H).

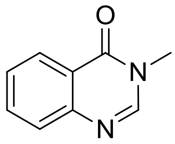


Org. Biomol. Chem. **2007**, *5*, 103–113.

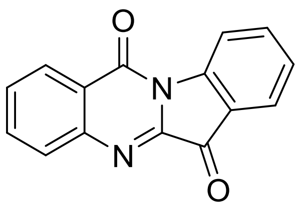
[1]H NMR (400 MHz, $CDCl_3$), δ 8.27 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.72 (td, *J* = 7.6, 2.0 Hz, 1H), 7.60 (d, *J* = 8.8 Hz, 1H), 7.43 (td, *J* = 7.6, 1,2 Hz, 1H), 4.09 (t, *J* = 6.0 Hz, 2H), 3.01 (t, *J* = 6.8 Hz, 2H), 2.04-1.94 (m, 4H).



[1]H NMR (400 MHz, $CDCl_3$), δ 8.25 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.70 (td, *J* = 7.6, 1.2 Hz, 1H), 7.26 (d, *J* = 8.0 Hz, 1H), 7.42 (td, *J* = 7.6, 1.2 Hz, 1H), 4.07 (t, *J* = 8.0 Hz, 2H), 2.81 (t, *J* = 8.0 Hz, 2H), 1.89-1.81 (m, 2H), 1.76-1.68 (m, 2H), 1.48-1.42 (m, 6H), 1.40-1.33 (m, 4H), 0.96-0.88 (m, 6H). EIMS 300 (M^+), HREIMS ($C_{19}H_{28}N_2O$) cacld. 300.2197, found 300.2200.

 *J. Am. Chem. Soc.* **2009**, *131*, 15996–15997.

[1]H NMR (400 MHz, $CDCl_3$), δ 8.33 (dd, *J* = 7.2, 1.6 Hz, 1H), 8.06 (s, 1H), 7.77 (td, *J* = 7.6, 1.6 Hz, 1H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.51 (td, *J* = 7.6, 1.6 Hz, 1H), 3.61 (s, 3H).



tryptanthrin *Tetrahedron Lett.* **2003**, *44*, 1883.

[1]H NMR (400 MHz, $CDCl_3$), δ 8.63 (d, *J* = 8.1 Hz, 1H), 8.44 (dd, *J* = 7.9, 0.7 Hz, 1H), 8.03 (d, *J* = 8.1 Hz, 1H), 7.92 (d, *J* = 7.5 Hz, 1H), 7.85 (t, *J* = 8.1 Hz, 1H), 7.79 (t, *J* = 7.5 Hz, 1H), 7.68 (t, *J* = 7.8 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 1H).

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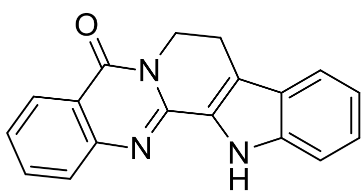
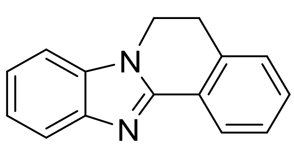
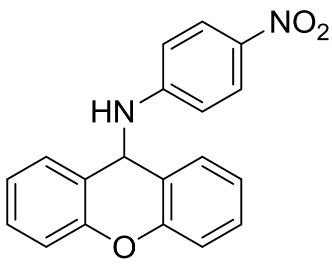


rutaecarpine *Tetrahedron* **2004**, *60*, 3417–3420.

[1]H NMR (400 MHz, $CDCl_3$), δ 9.48 (s, 1H), 8.32 (d, *J* = 7.8 Hz, 1H), 7.70-7.62 (m, 3H), 7.40 (t, *J* = 7.9 Hz, 1H), 7.37 (d, *J* = 8.2 Hz, 1H), 7.31 (t, *J* = 7.5 Hz, 1H), 7.18 (t, *J* = 7.7 Hz, 1H), 4.59 (t, *J* = 6.8 Hz, 2H), 3.23 (t, *J* = 6.8 Hz, 2H).

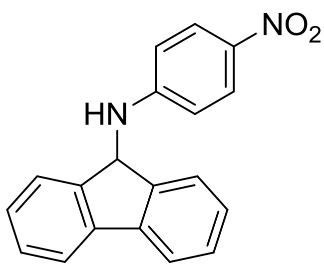
 *Tetrahedron* **2006**, *62*, 4306–4316.

[1]H NMR (400 MHz, $CDCl_3$), δ 8.27 (d, *J* = 7.6 Hz, 1H), 7.80 (d, *J* = 7.6 Hz, 1H), 7.38-7.21 (m, 6H), 4.22 (t, *J* = 6.9 Hz, 2H), 3.19 (t, *J* = 6.9 Hz, 2H).



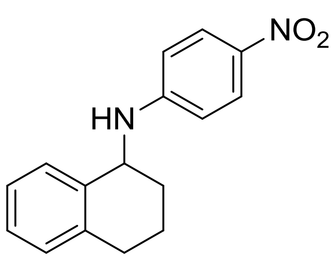
Chem. Eur. J. **2010**, *16*, 10494–10501.

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.16 (d, *J* = 9.1 Hz, 1H), 8.04 (d, *J* = 9.1 Hz, 2H), 7.4 (m, 4H), 7.25 (m, 2H), 7.15 (m, 2H), 6.95 (d, *J* = 9.1 Hz, 1H), 6.32 (d, *J* = 9.1 Hz, 1H).



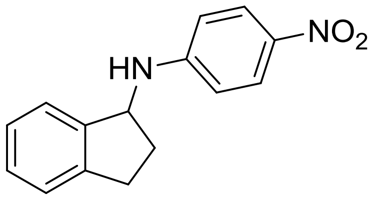
Chem. Eur. J. **2010**, *16*, 10494–10501.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.0 Hz, 2H), 7.74 (d, *J* = 7.1 Hz, 2H), 7.54 (d, *J* = 7.1 Hz, 2H), 7.45 (m, 2H), 7.30 (m, 2H), 6.68 (d, *J* = 8.0 Hz, 2H), 5.72 (s, 1H), 4.97 (br s, 1H).



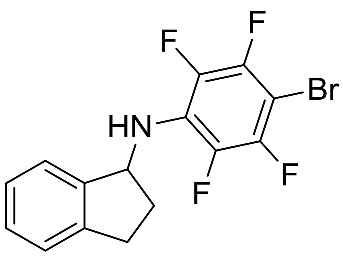
Chem. Eur. J. **2010**, *16*, 10494–10501.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.10 (d, *J* = 9.1 Hz, 2H), 7.20 (m, 4H), 6.60 (d, *J* = 9.1 Hz, 2H), 4.74 (m, 1H), 2.85 (m, 2H), 2.06 (m, 2H), 1.85 (m, 2H).

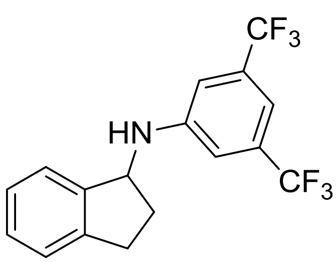


Adv. Synth. Catal. **2013**, *355*, 181–190.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.8 Hz, 2H), 7.35-7.30 (m, 3H), 7.28-7.22 (m, 1H), 6.65 (d, *J* = 8.8 Hz, 2H), 5.10 (q, *J* = 6.8Hz, 1H), 4.73 (d, *J* = 6.8 Hz, 1H), 3.11-3.03 (m, 1H), 2.99-2.91 (m, 1H), 2.68-2.60 (m, 1H), 2.01-1.92 (m, 1H).

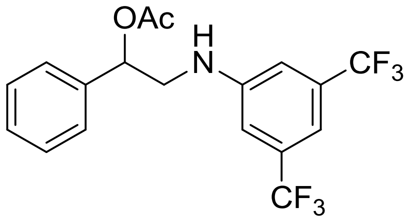


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 7.0 Hz, 1H), 7.27-7.20 (m, 3H), 5.30 (q, *J* = 8.2 Hz, 1H), 4.01 (d, *J* = 8.2 Hz, 1H), 3.07-3.00 (m, 1H), 2.93-2.84 (m, 1H), 2.60-2.55 (m, 1H), 1.95-1.87 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 146.14 (m), 144.56 (m), 143.55, 143.33, 138.52 (m), 136.92 (m), 128.44, 126.97, 125.04, 124.13, 60.72 (t, *J* = 3.9 Hz), 35.15, 29.98. EIMS 359 (M^+), HREIMS ($C_{15}H_{10}BrF_4N$) cacld. 358.9927, found 358.9929.

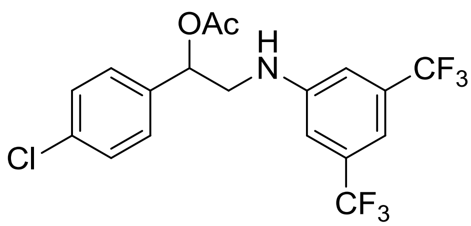


J. Porphyrins Phthalocyanines **2010**, *14*, 732–740.

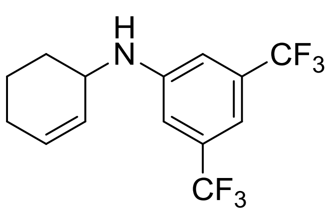
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.25 (m, 4H), 7.17 (s, 1H), 7.03 (s, 2H), 5.05 (q, *J* = 6.9 Hz, 1H), 4.35 (d, *J* = 6.9 Hz, 1H), 3.10-3.00 (m, 1H), 2.99-2.90 (m, 1H), 2.67-2.61 (m, 1H), 1.97-1.90 (m,1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.31, 143.62, 143.08, 132.59 (q, *J* = 32.6 Hz), 128.50, 127.68, 126.98, 125.16, 124.07, 123.62 (q, *J* = 271.1 Hz), 112.12 (d, *J* = 3.0 Hz), 110.20 (quint, *J* = 3.9 Hz), 58.42, 33.46, 30.25. EIMS 345 (M^+), HREIMS ($C_{17}H_{13}F_6N$) cacld. 345.0947, found 345.0950.



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (m, 5H), 7.15 (s, 1H), 6.95 (s, 2H), 5.94 (dd, *J* = 7.3, 4.7 Hz, 1H), 4.42 (brs 1H), 3.64-3.60 (m, 1H), 3.52-3.50 (m, 1H), 2.09 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.58, 148.32, 137.54, 132.32 (q, *J* = 32.4 Hz), 128.86, 128.73, 126.58, 125.16, 124.07, 123.53 (q, *J* = 270.9 Hz), 112.03 (d, *J* = 3.1 Hz), 110.20 (quint, *J* = 4.0 Hz), 74.55, 48.73, 21.00. EIMS 391 (M^+), HREIMS ($C_{18}H_{15}F_6NO_2$) cacld. 391.1002, found 391.1004.

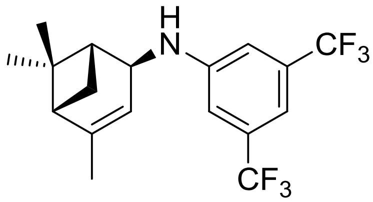


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.4 Hz, 2H), 7.17 (s, 1H), 6.96 (s, 2H), 5.91 (dd, *J* = 7.2, 4.8 Hz, 1H), 4.36 (brs 1H), 3.64-3.58 (m, 1H), 3.52-3.49 (m, 1H), 2.10 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.39, 148.10, 136.07, 134.65， 132.51 (q, *J* = 32.6 Hz), 129.09, 127.88, 123.48 (q, *J* = 271.1 Hz), 112.05 (d, *J* = 3.0 Hz), 110.80 (t, *J* = 3.8 Hz), 73.87, 48.60, 21.00. EIMS 425 (M^+), HREIMS ($C_{18}H_{14}ClF_6NO_2$) cacld. 425.0612, found 425.0611.

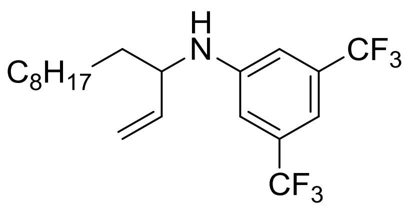


Tetrahedron **2004**, *60*, 4989–4994.

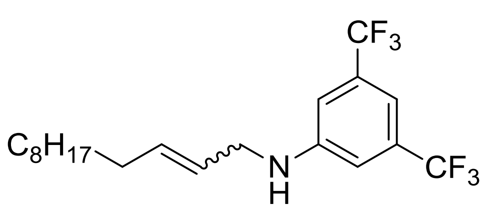
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (s, 1H), 6.93 (s 2H), 5.92 (m, 1H), 5.70 (m, 1H), 4.10 (brs, 1H), 4.03 (brs, 1H), 2.05 (brs, 2H), 1.92 (m, 1H), 1.74-1.62 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.78, 132.65 (q, *J* = 32.4 Hz), 131.47, 126.99, 123.63 (q, *J* = 271.0 Hz), 112.05 (d, *J* = 3.2 Hz), 109.84 (t, *J* = 3.8 Hz), 47.77, 28.45, 25.00, 19.42. EIMS 309 (M^+), HREIMS ($C_{14}H_{13}F_6N$) cacld. 309.0947, found 309.0949.



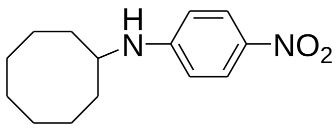
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (s, 1H), 6.90 (s 2H), 5.28 (s, 1H), 4.18 (d, *J* = 7.6 Hz, 1H), 4.13 (m, 1H), 2.32-2.24 (m, 2H), 2.09 (t, *J* = 5.4 Hz, 1H), 1.74 (s, 3H), 1.36 (s, 3H), 1.22 (d, *J* = 9.0 Hz, 1H), 0.99 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.43, 147.91, 132.29 (q, *J* = 32.2 Hz), 123.64 (q, *J* = 271.1 Hz), 116.00, 111.98, 109.68 (t, *J* = 3.9 Hz), 52.71, 47.71, 44.11, 43.92, 27.87, 26.48, 22.80, 20.54. EIMS 363 (M^+), HREIMS ($C_{18}H_{19}F_6N$) cacld. 363.1417, found 363.1414.



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07 (s, 1H), 6.92 (s 2H), 5.74-5.64 (m, 1H), 5.20 (d, *J* = 15.8 Hz, 1H), 5.17 (d, *J* = 9.8 Hz, 1H), 4.10 (brs, 1H), 3.82 (brs, 1H), 1.67-1.59 (m, 2H), 1.44-1.23 (brs, 12H), 0.88 (t, *J* = 6.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.13, 138.46, 132.59 (q, *J* = 32.2 Hz), 123.54 (q, *J* = 271.1 Hz), 115.98, 112.38, 109.96 (t, *J* = 3.8 Hz), 55.95, 35.71, 31.89, 29.74, 29.53, 29.46, 29.31, 25.83, 22.70, 14.14. EIMS 395 (M^+), HREIMS ($C_{20}H_{27}F_6N$) cacld. 395.2043, found 395.2045.

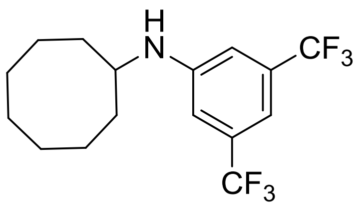


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (s, 1H), 6.93 (s 2H), 5.76-5.64 (m, 1H), 5.53-5.30 (m, 1H), 4.19 (brs, 0.7H), 4.10 (brs, 0.3H), 3.80 (brs, 0.6H), 3.75 (brs, 1.4H), 2.17-2.10 (m, 0.6H), 2.07-2.02 (m, 1.4H), 1.26 (brs, 12H), 0.87 (t, *J* = 6.5 Hz, 3H). EIMS 395 (M^+), HREIMS ($C_{20}H_{27}F_6N$) cacld. 395.2043, found 395.2045.

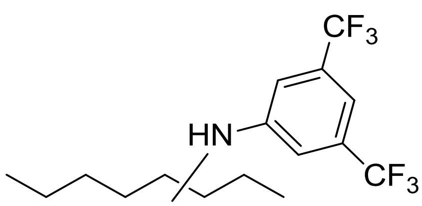


Chem. Eur. J. **2010**, *16*, 10494–10501.

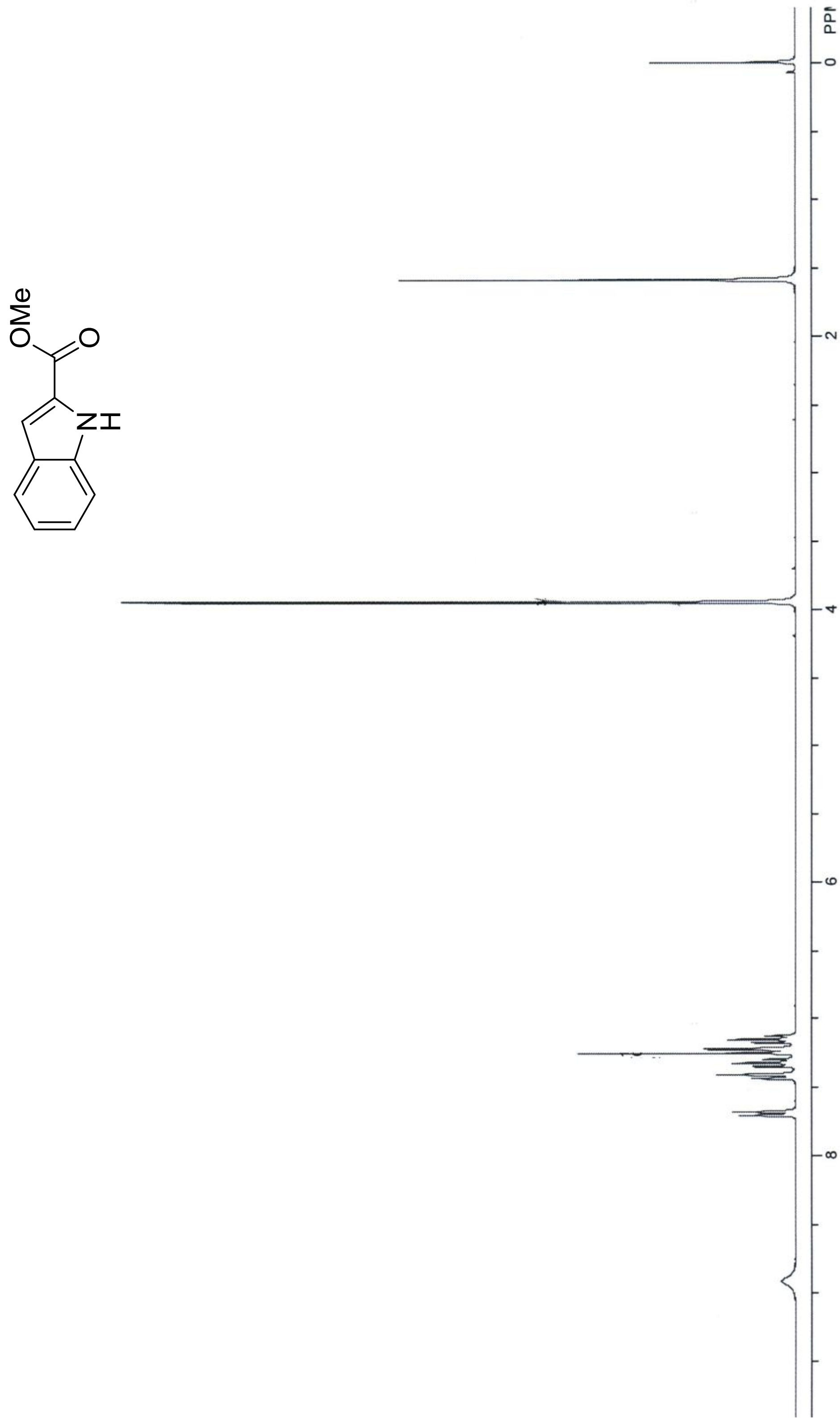
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 9.2 Hz, 2H), 6.45 (d, *J* = 9.2 Hz, 2H), 4.45 (br s, 1H), 3.59 (m, 1H), 1.92 (m, 2H), 1.75 (m, 2H), 1.66-1.40 (m, 10H).



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 (s, 1H), 6.85 (s 2H), 4.04 (d, *J* = 6.5 Hz, 1H), 3.54 (m, 1H), 1.92-1.85 (m, 2H), 1.76-1.71 (m, 2H), 1.66-1.55 (brs, 10H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.73, 132.41 (q, *J* = 32.3 Hz), 123.66 (q, *J* = 270.9 Hz), 112.05, 109.42 (t, *J* = 3.9 Hz), 52.55, 33.65, 27.06, 25.78, 23.82. EIMS 339 (M^+), HREIMS ($C_{16}H_{19}F_6N$) cacld. 339.1417, found 339.1418.



^{1}H NMR (300 MHz, $CDCl_3$) δ 7.08 (s, 1H), 6.88 (s 2H), 3.88 (brs, 1H), 3.53-3.30 (m, 1H), 1.64-1.20 (m, 10H), 0.96-0.86 (m, 6H). EIMS 339 (M^+), HREIMS ($C_{16}H_{19}F_6N$) cacld. 339.1417, found 339.1418. EIMS 341 (M^+), HREIMS ($C_{16}H_{21}F_6N$) cacld. 341.1573, found 341.1575.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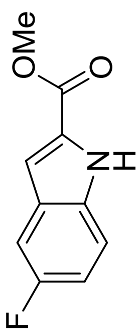
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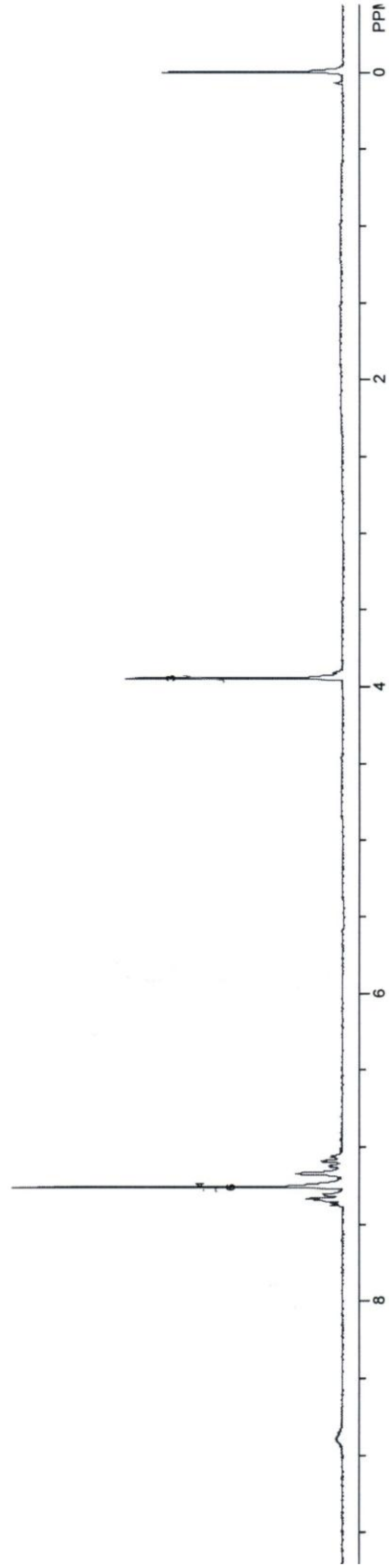
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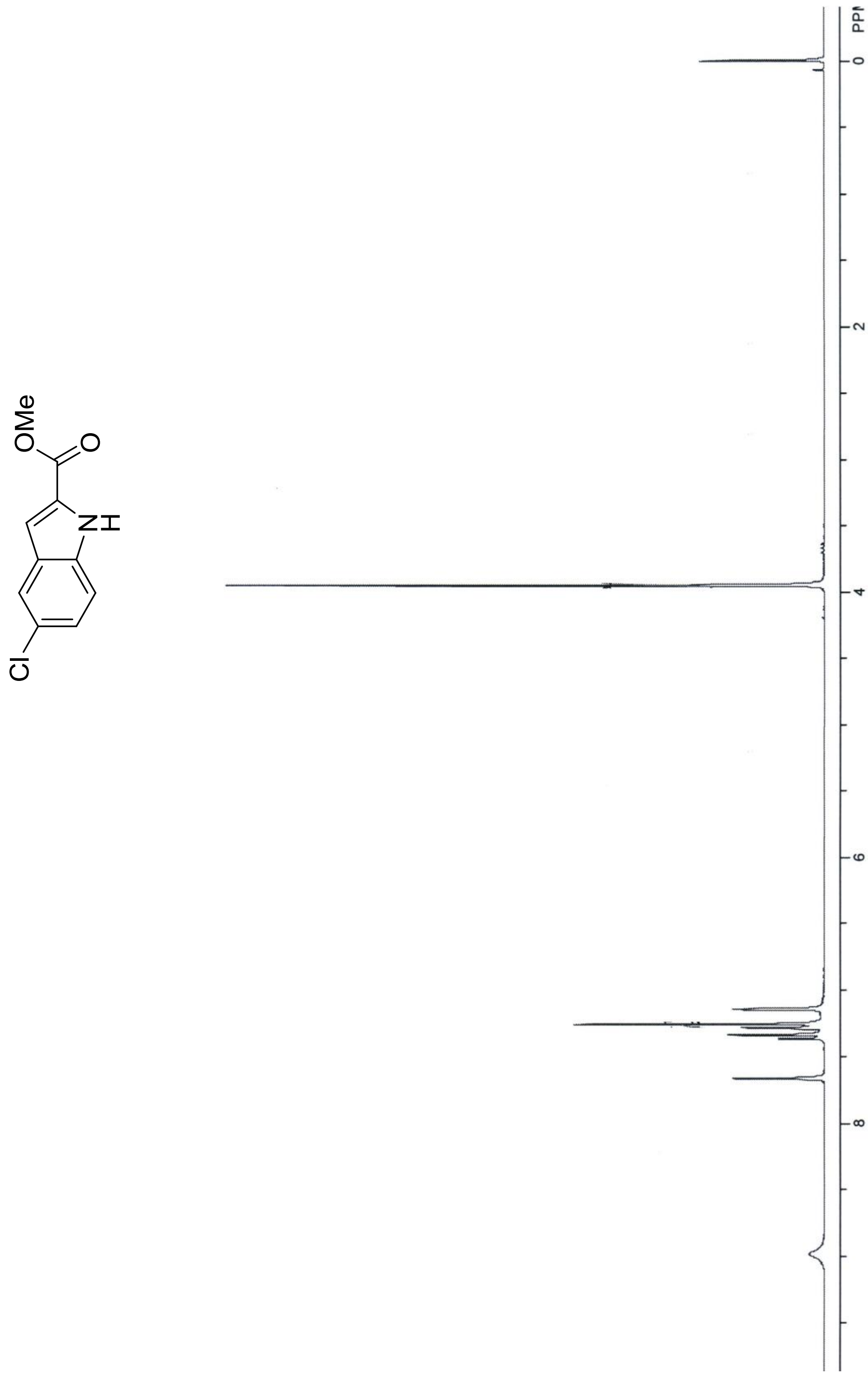

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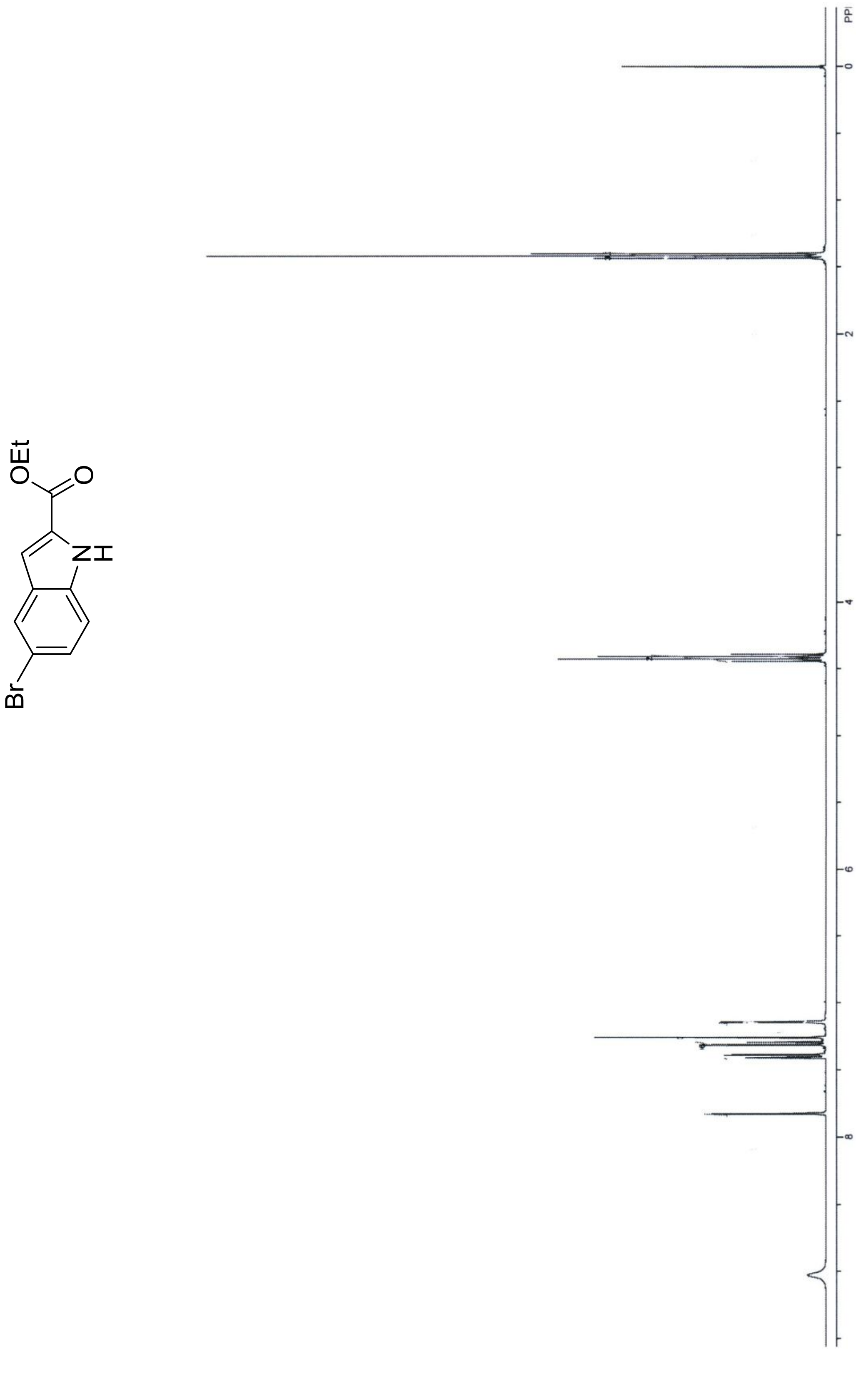
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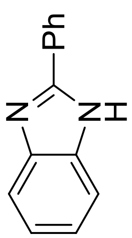
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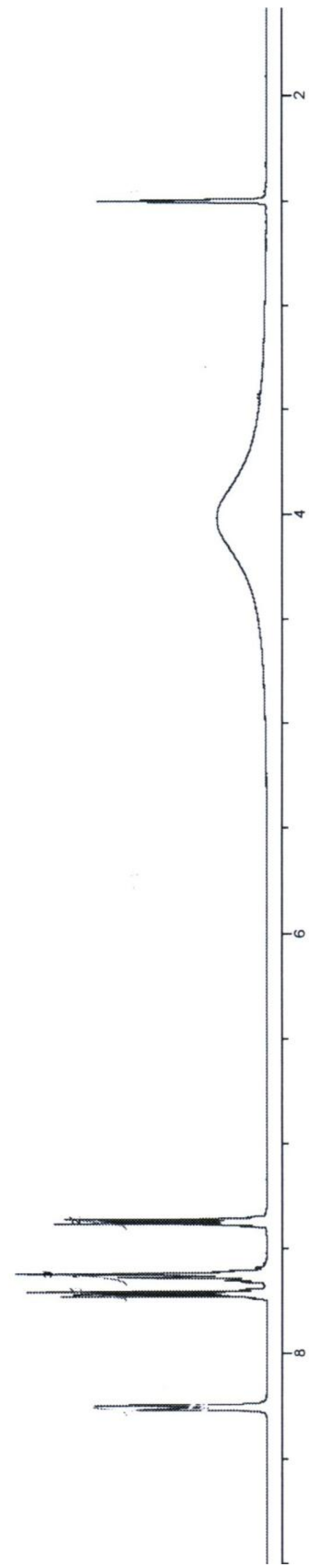
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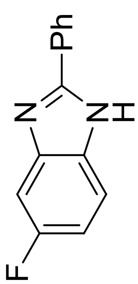
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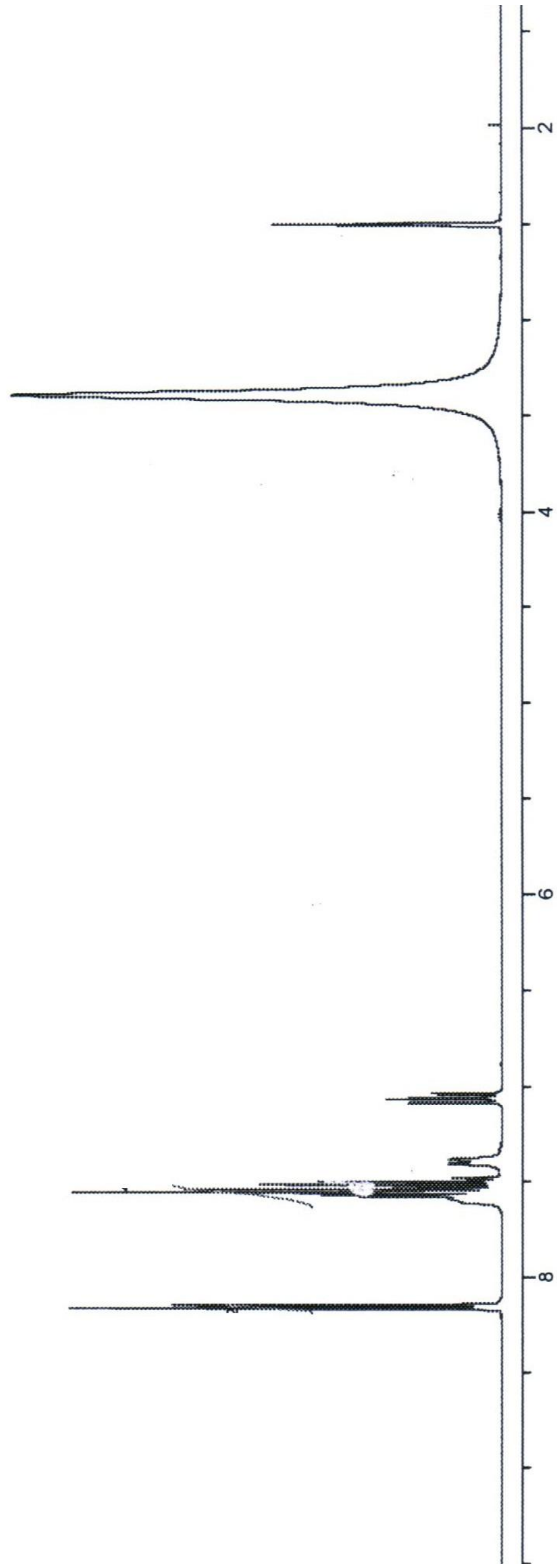
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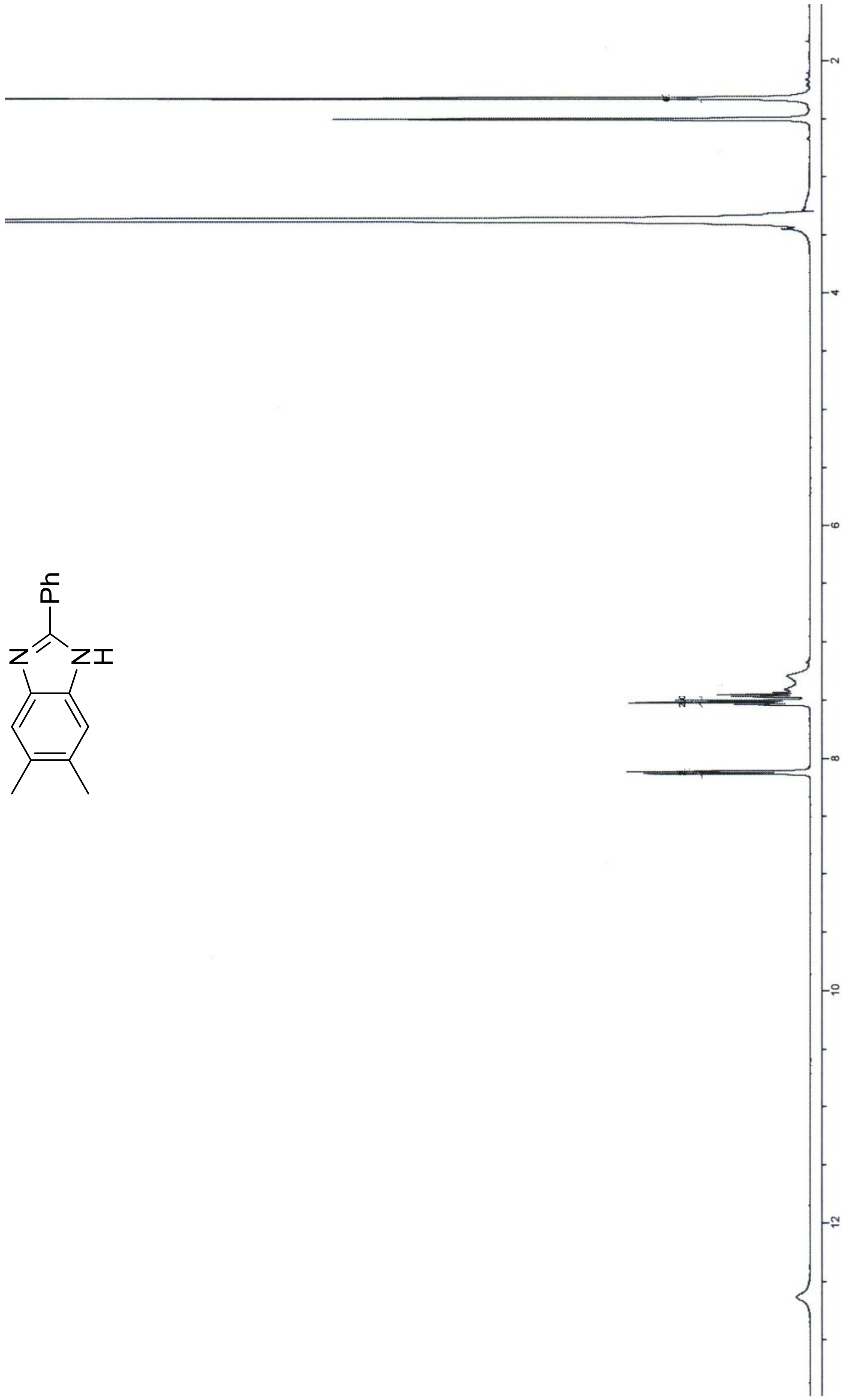
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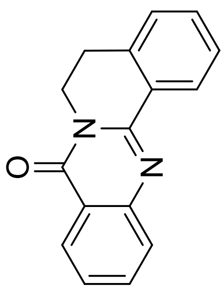
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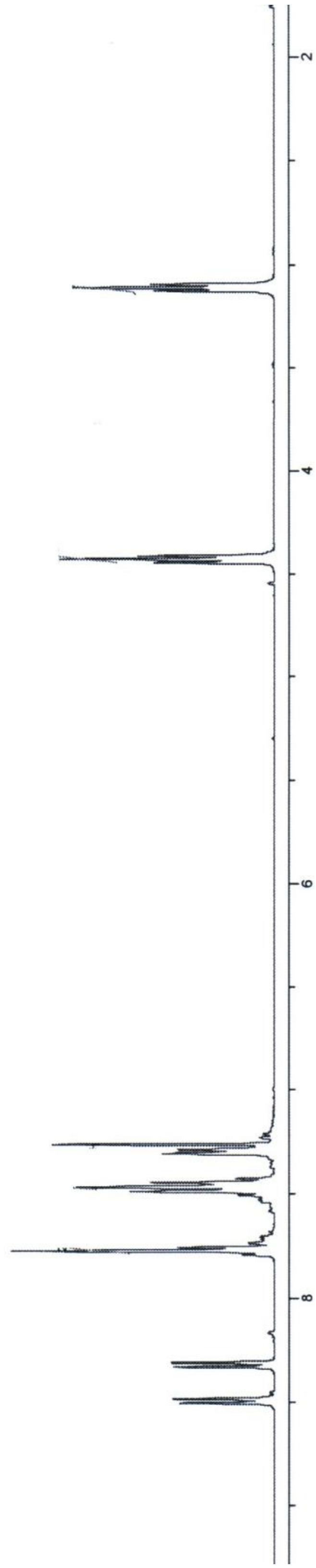
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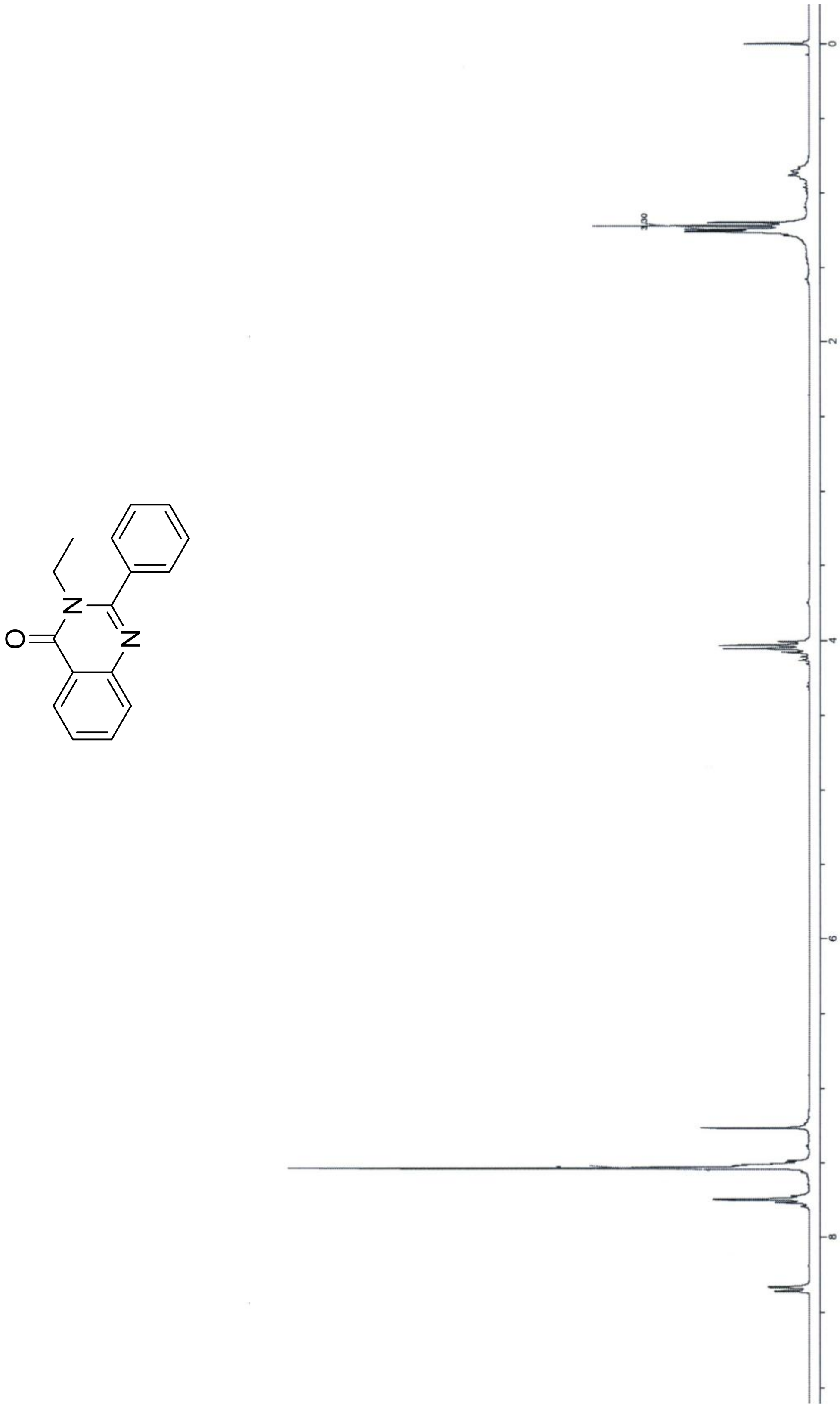

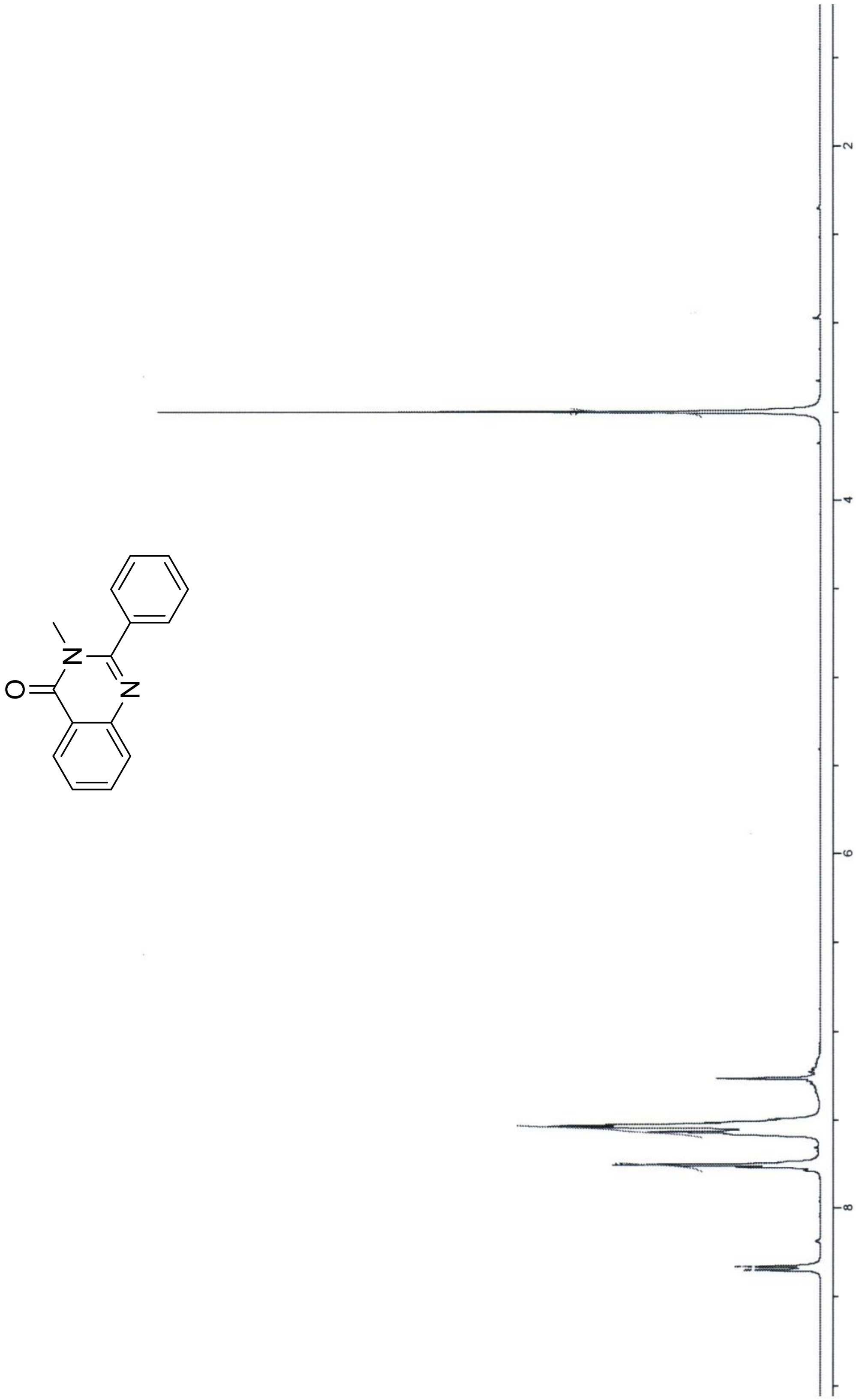
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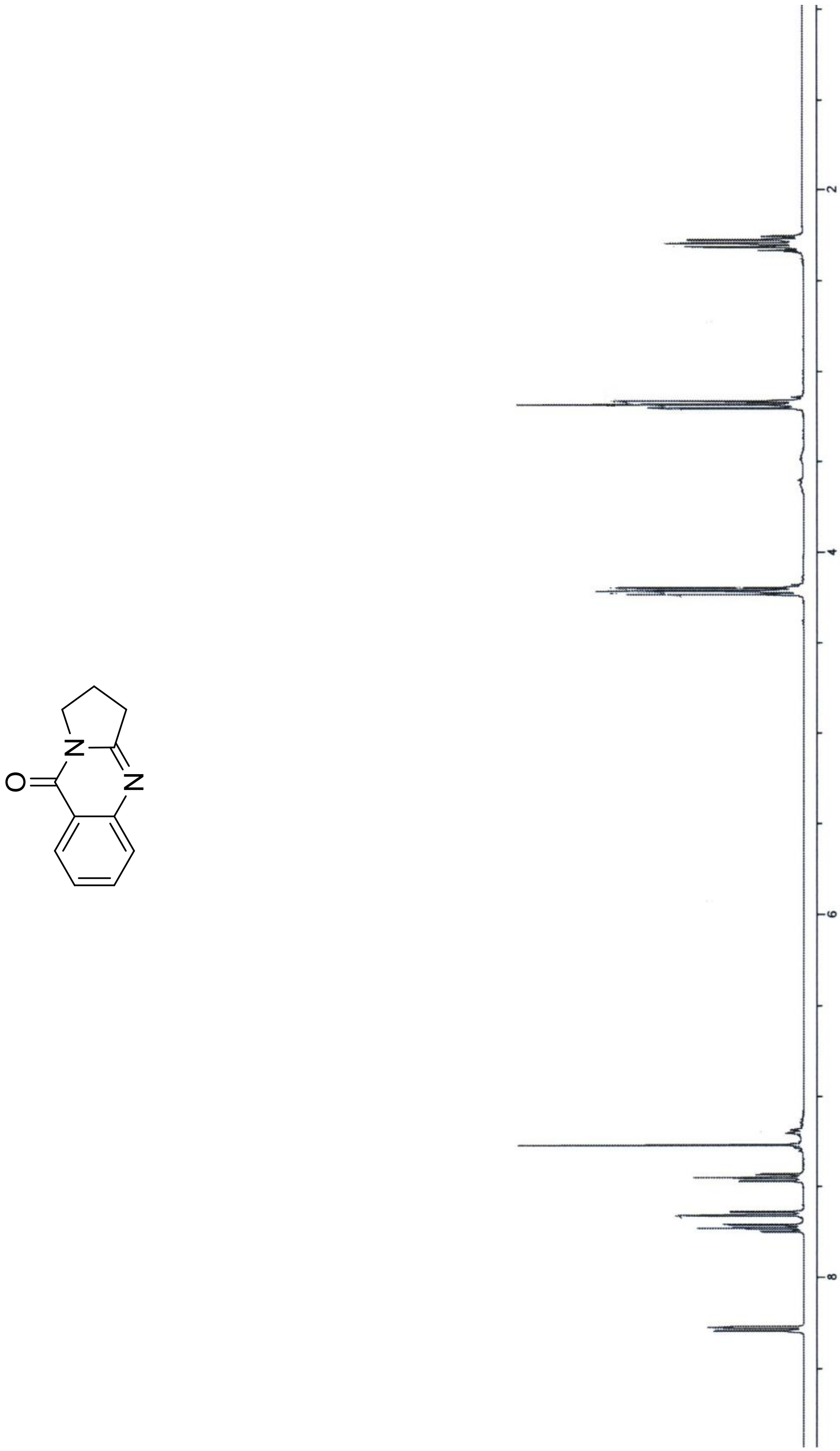
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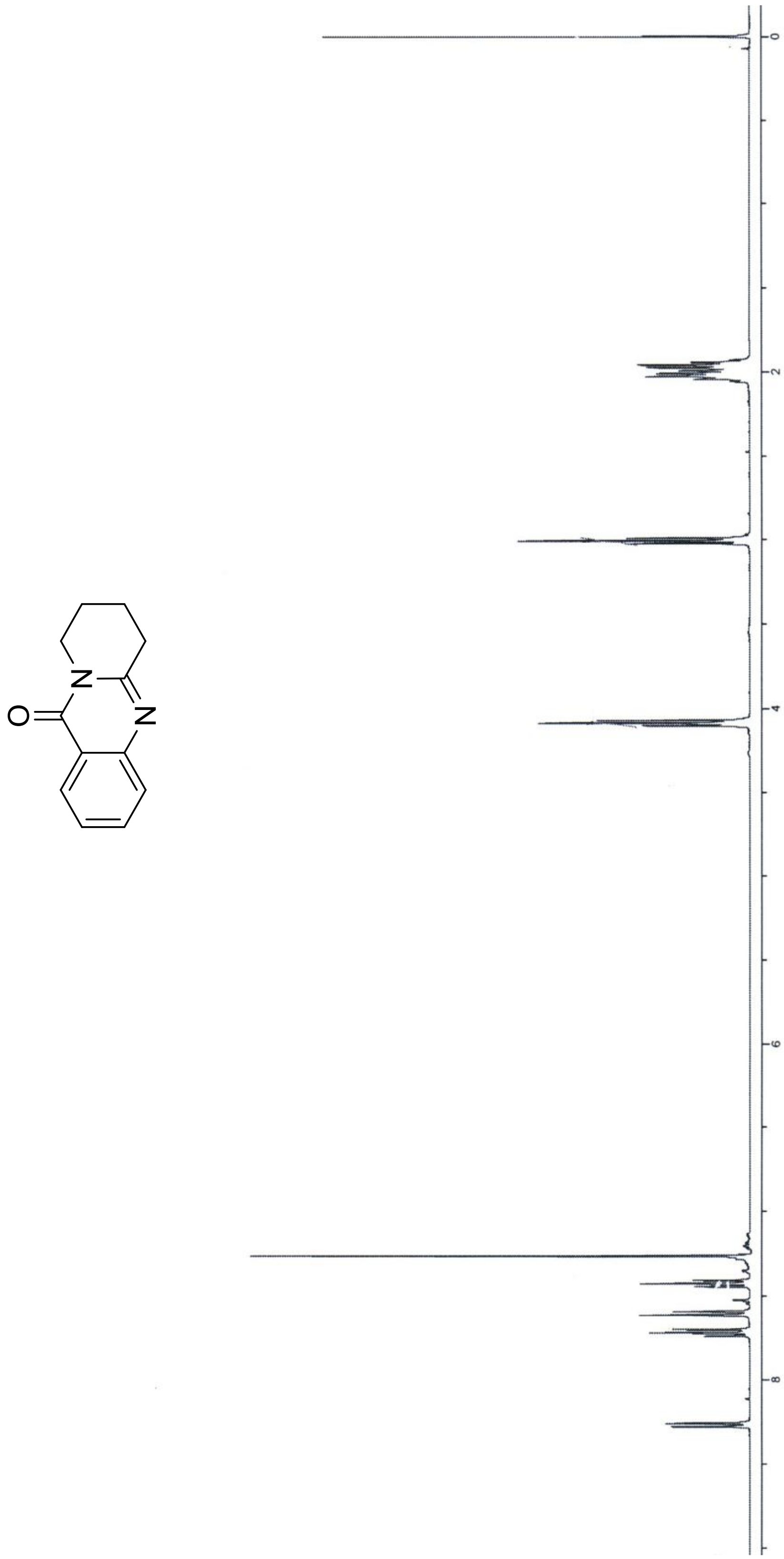

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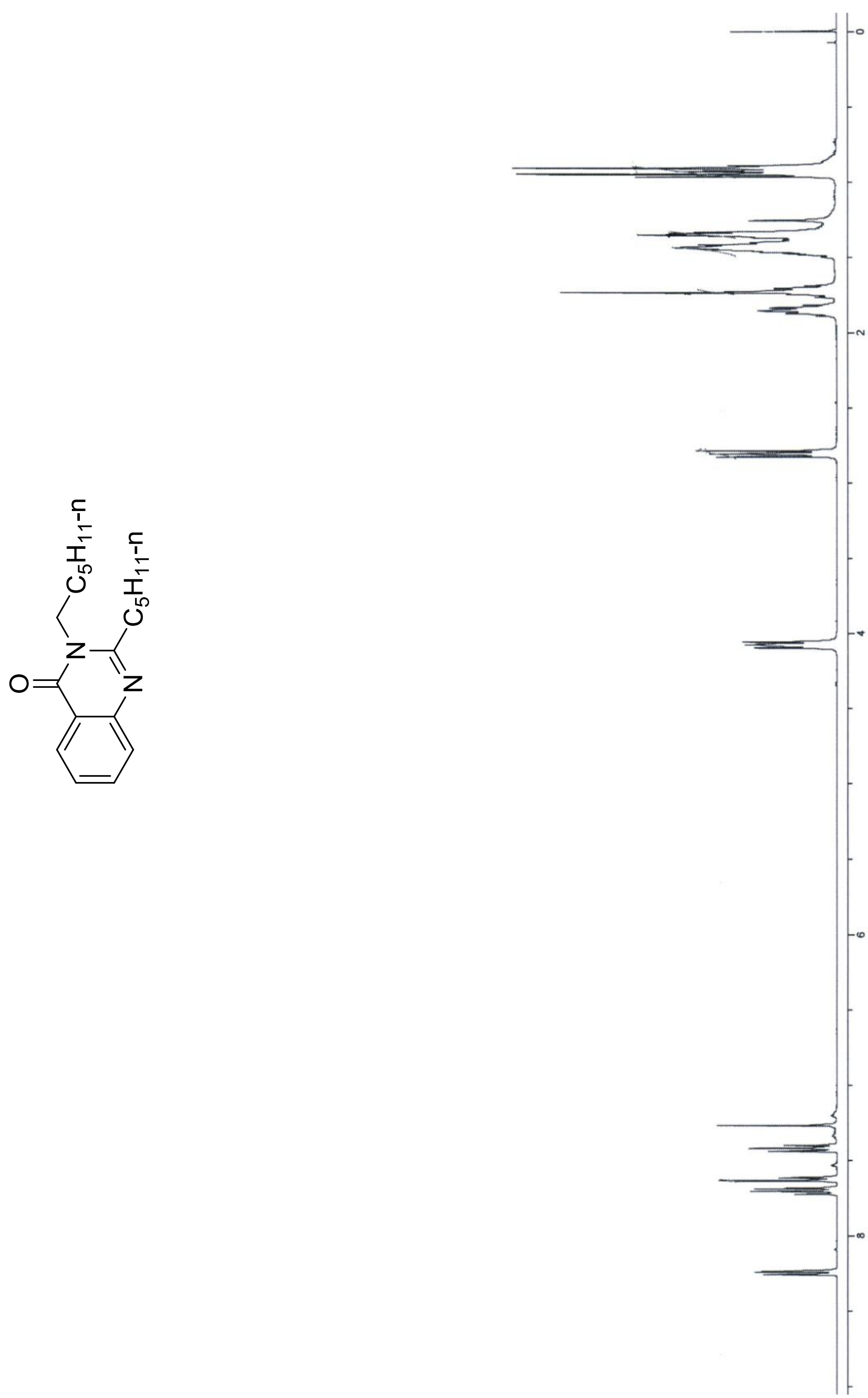

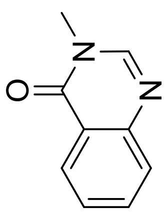

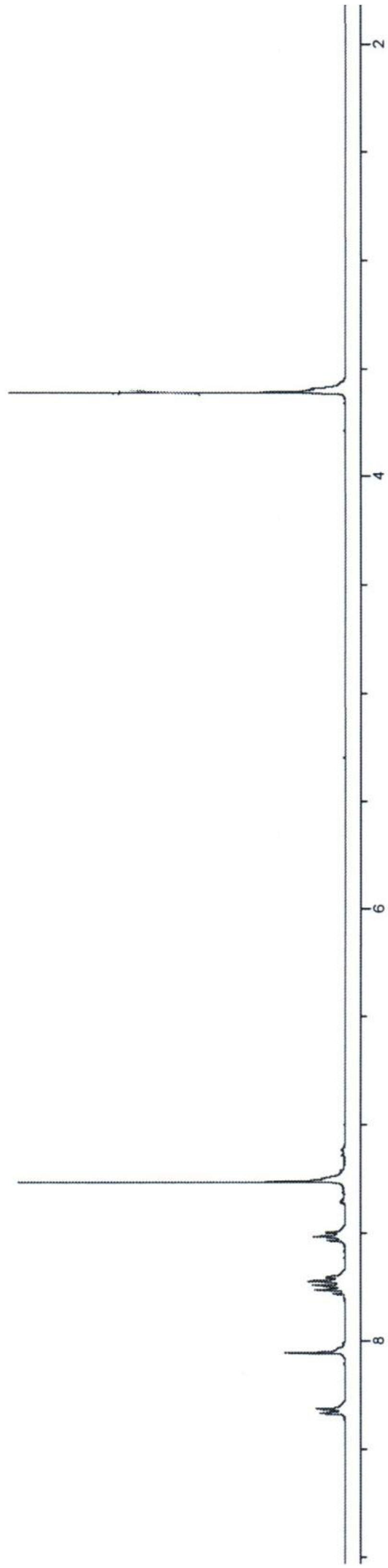

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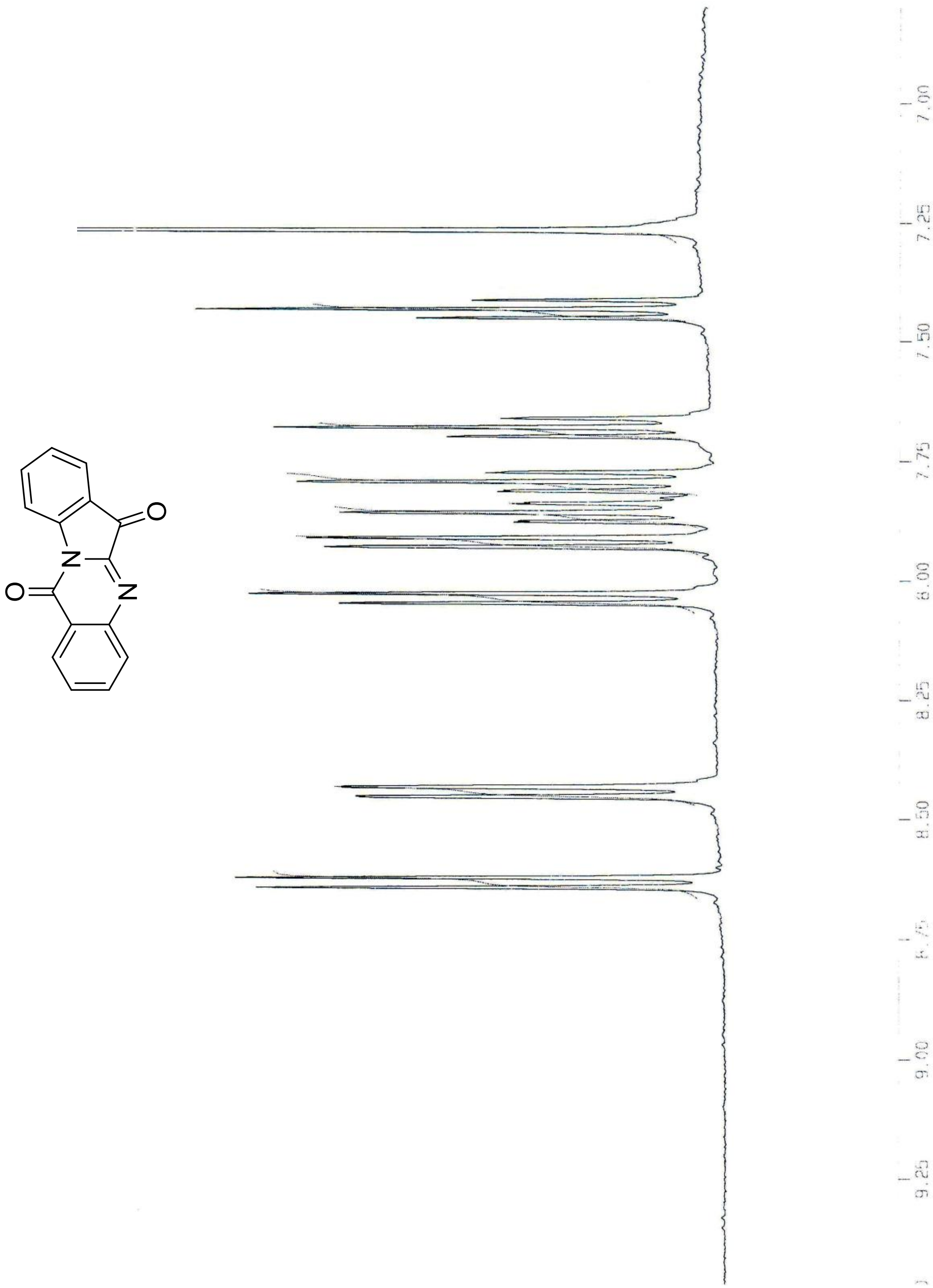
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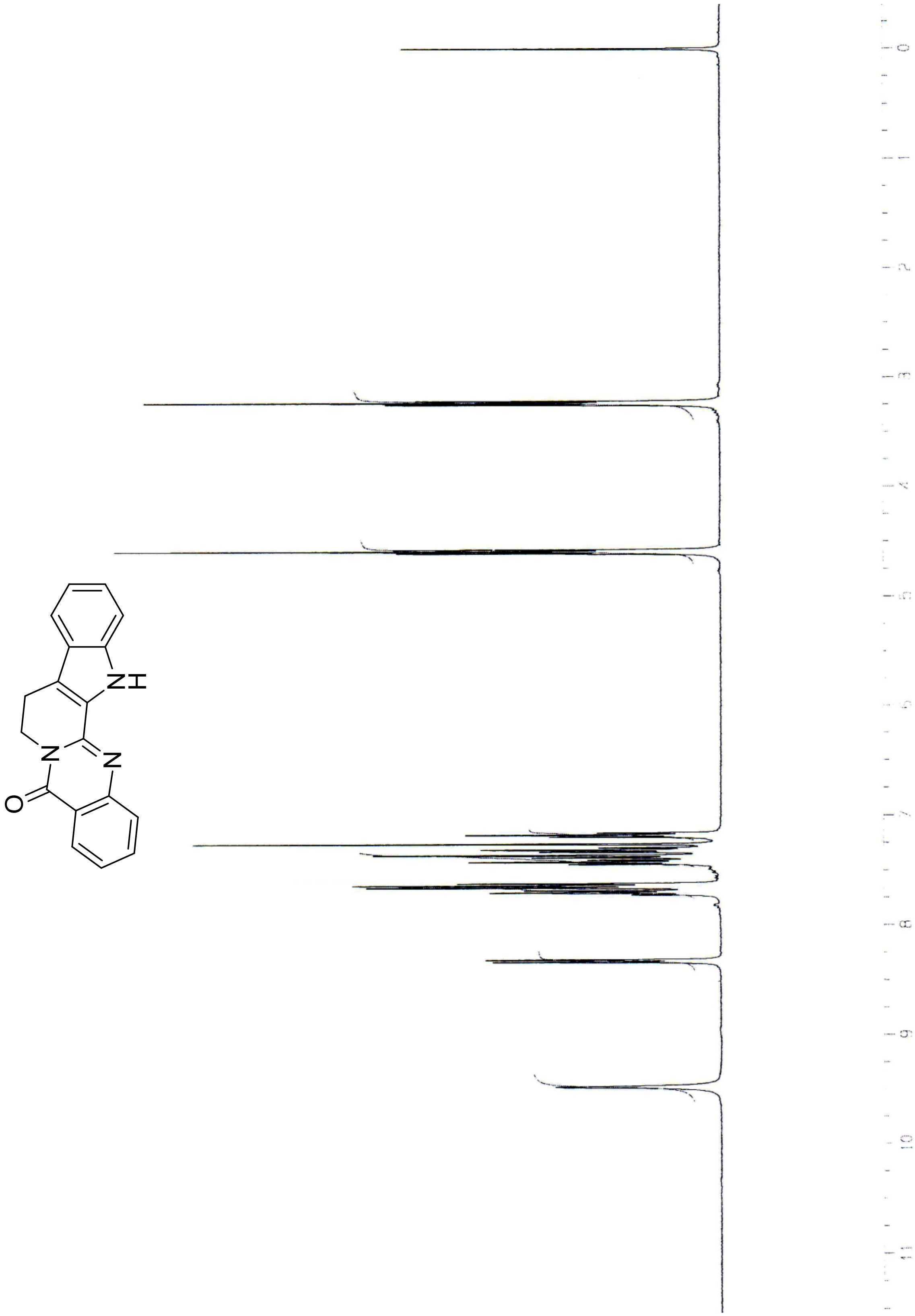

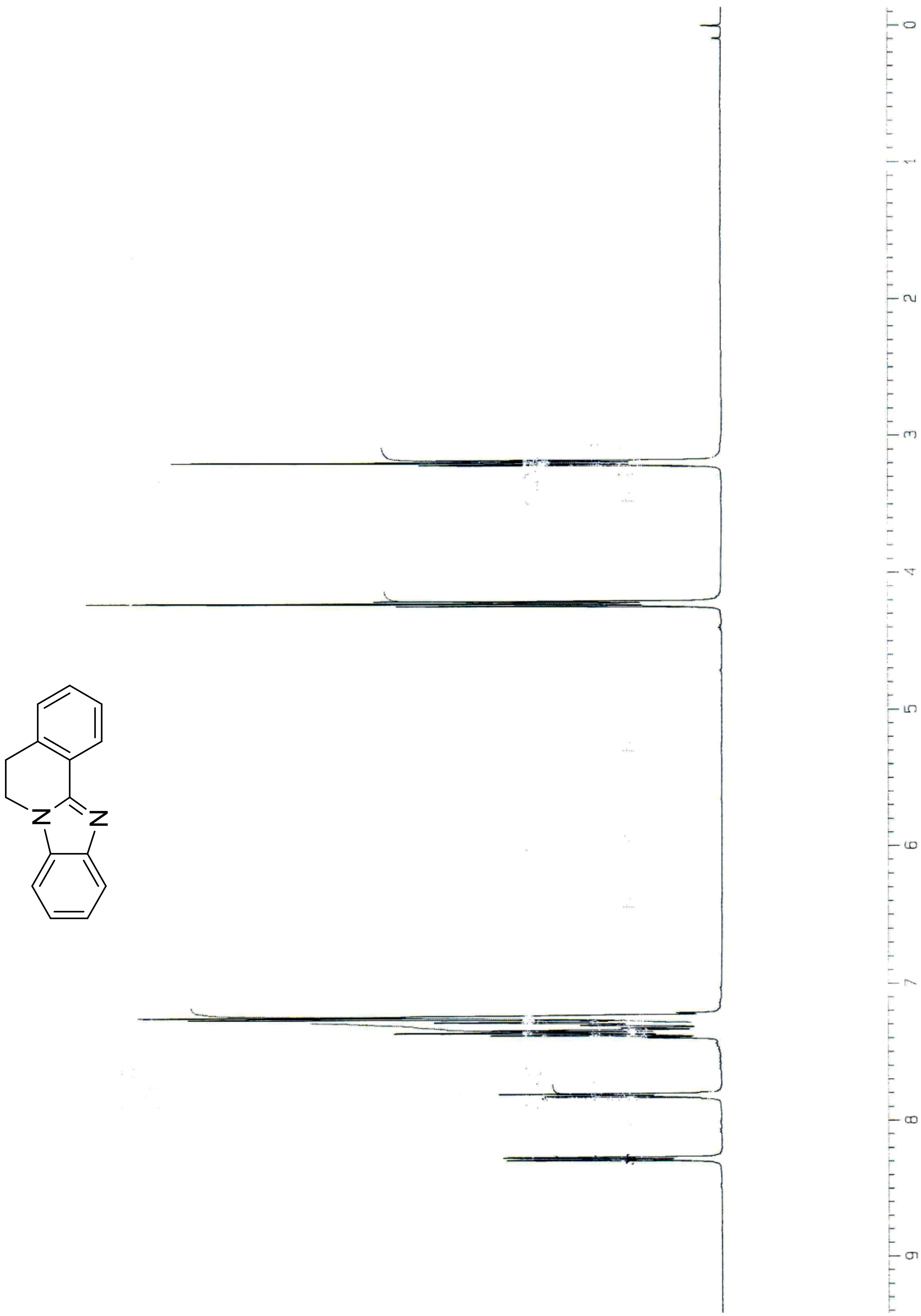

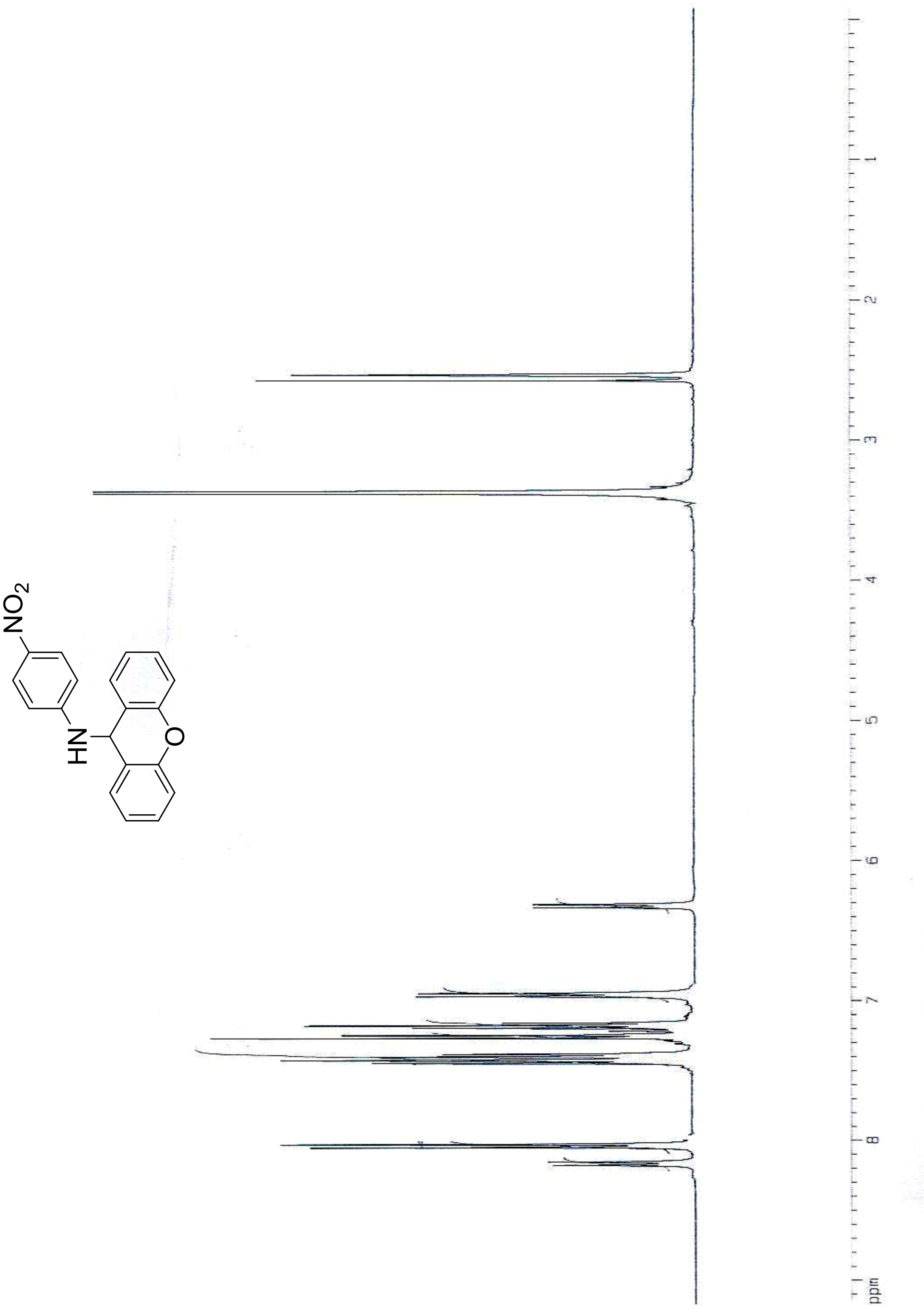
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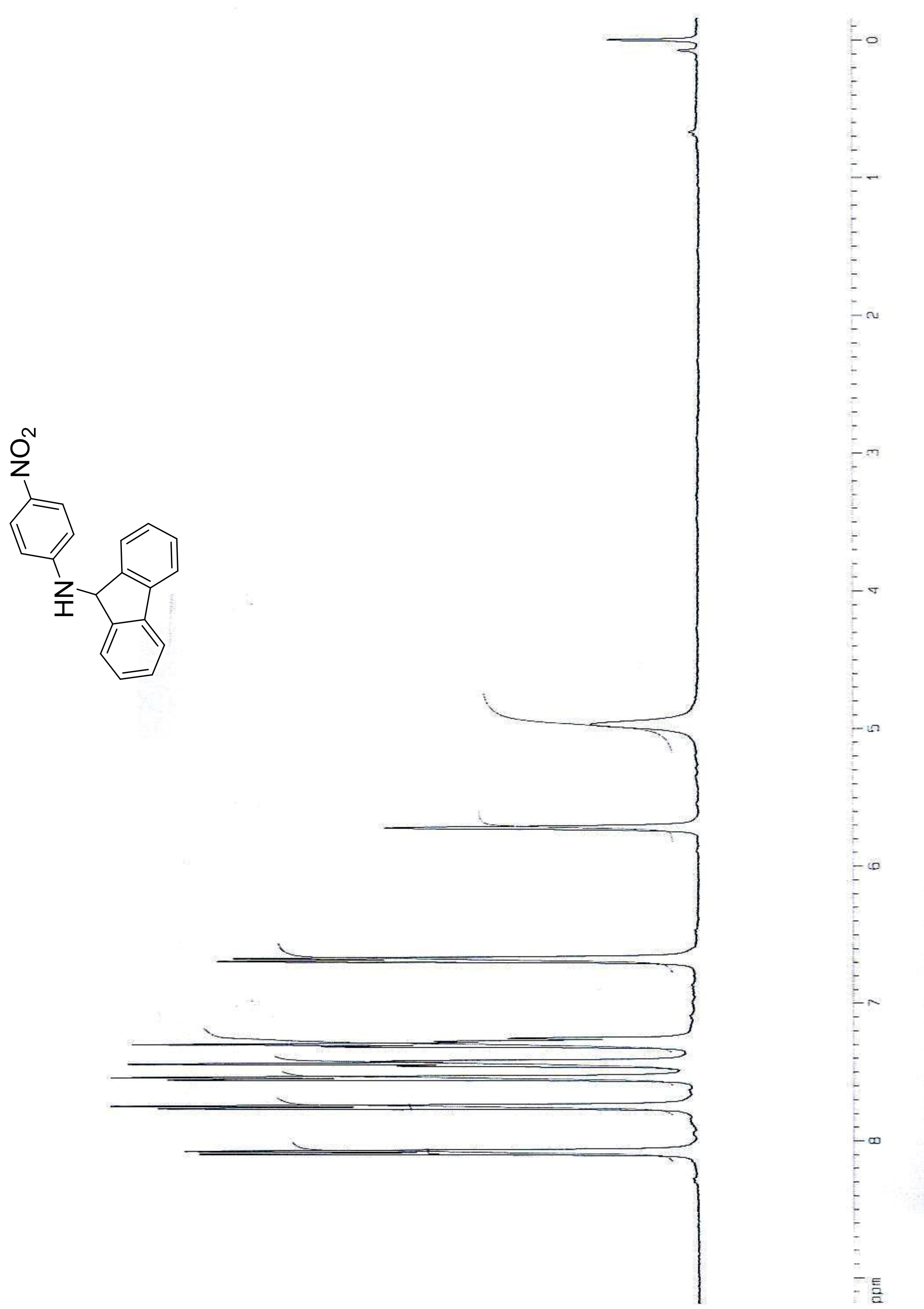
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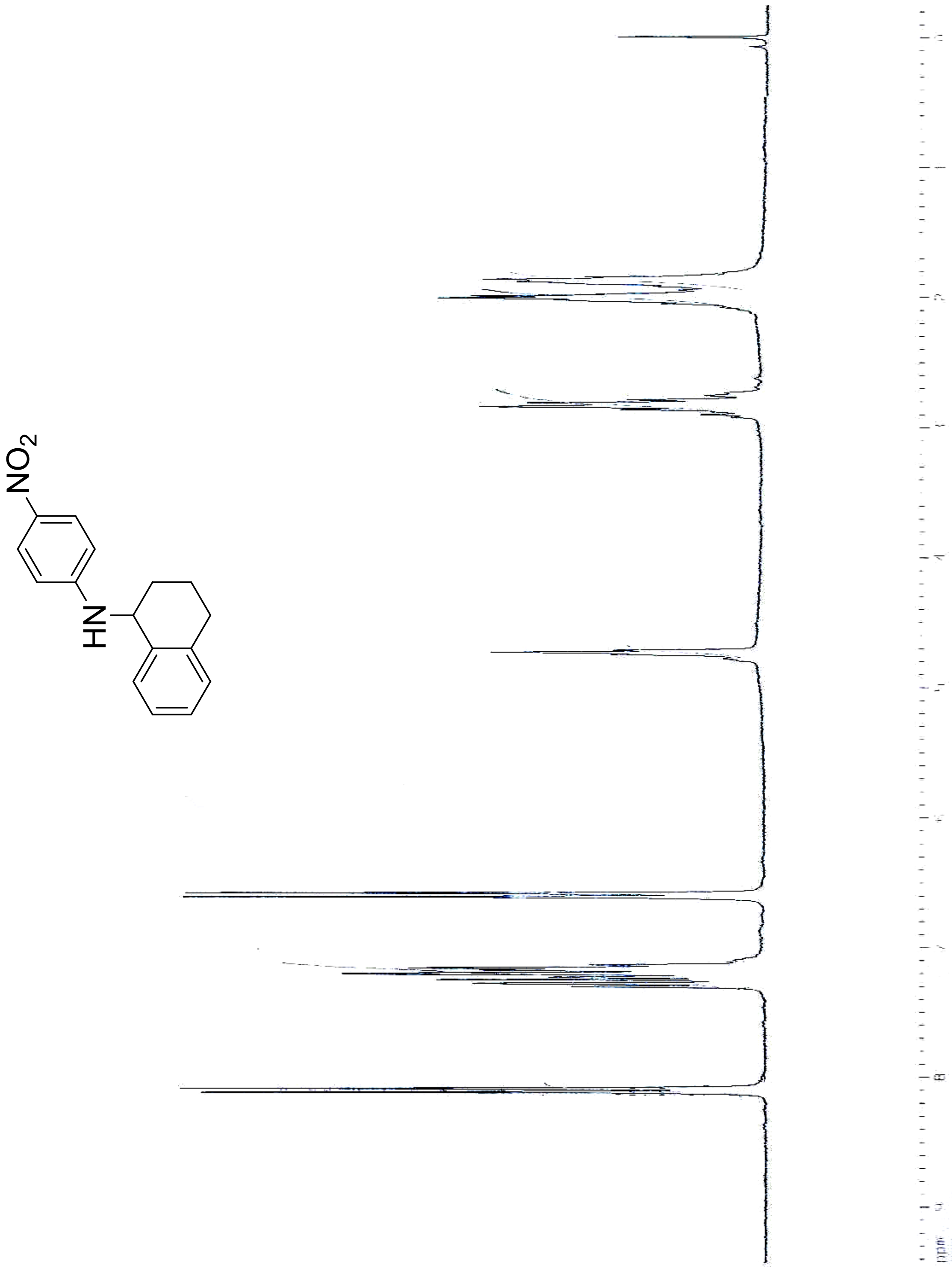

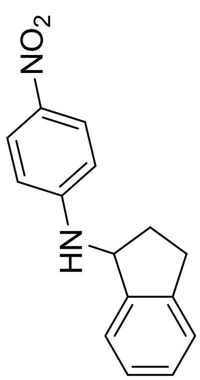
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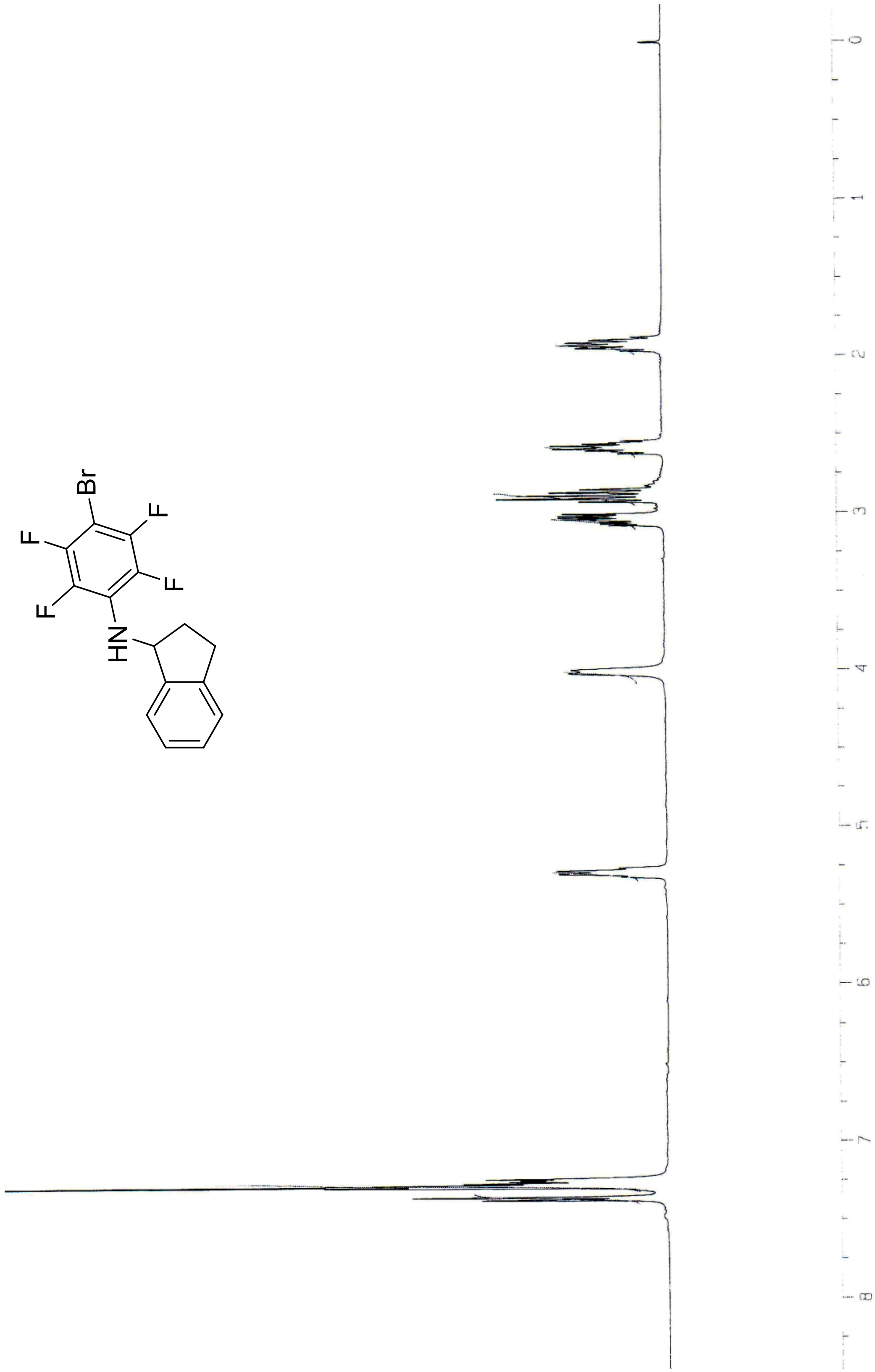
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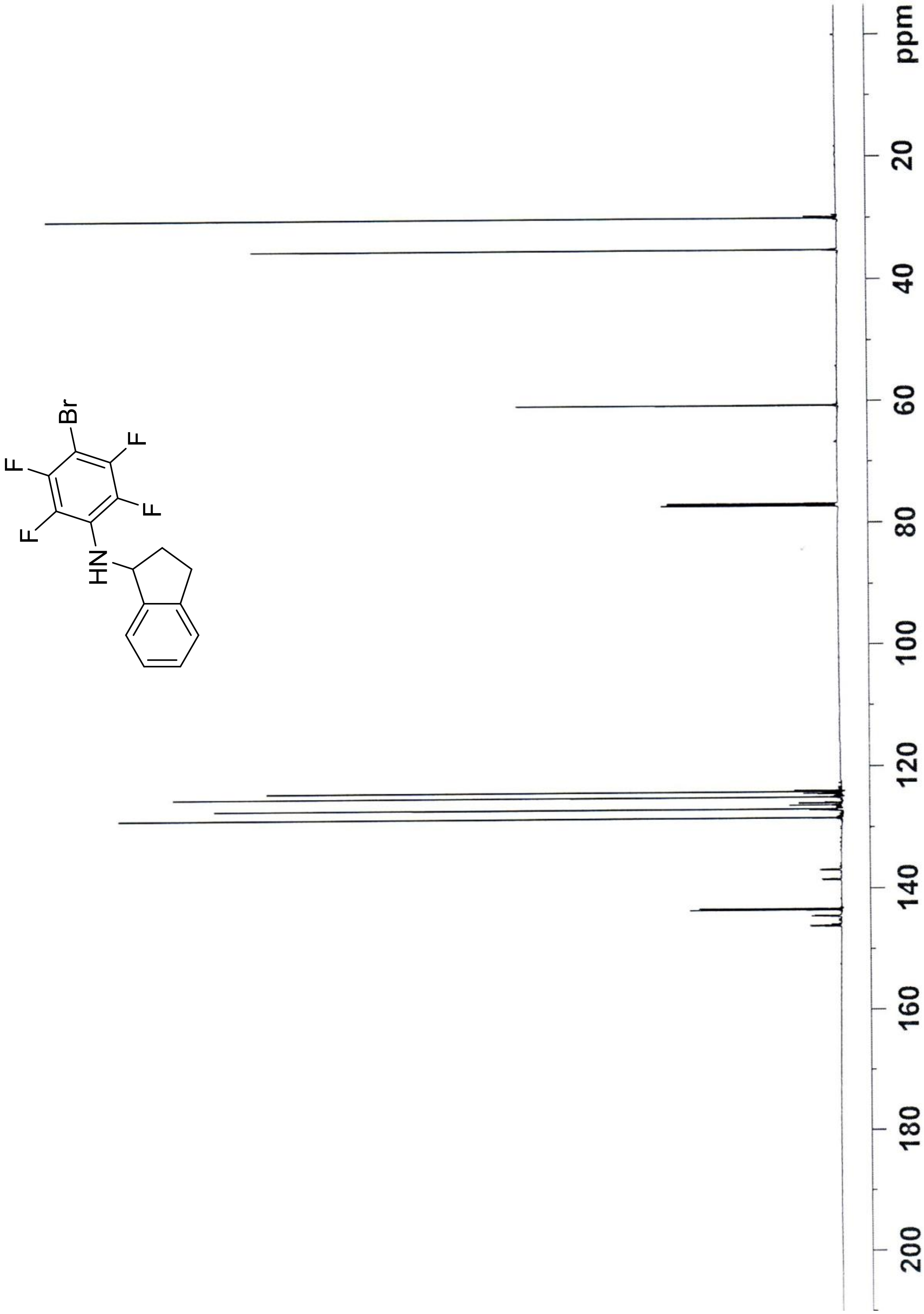
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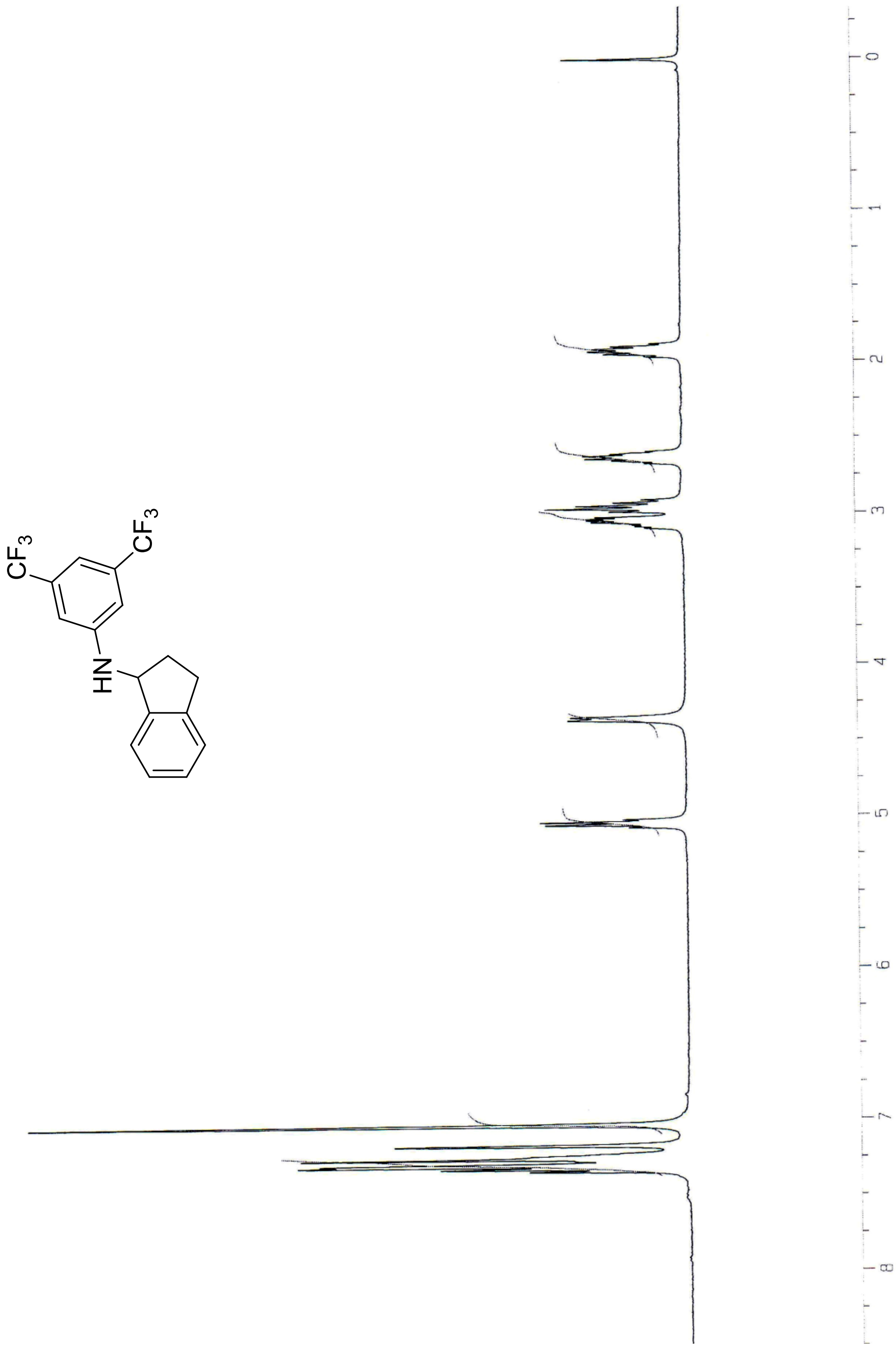

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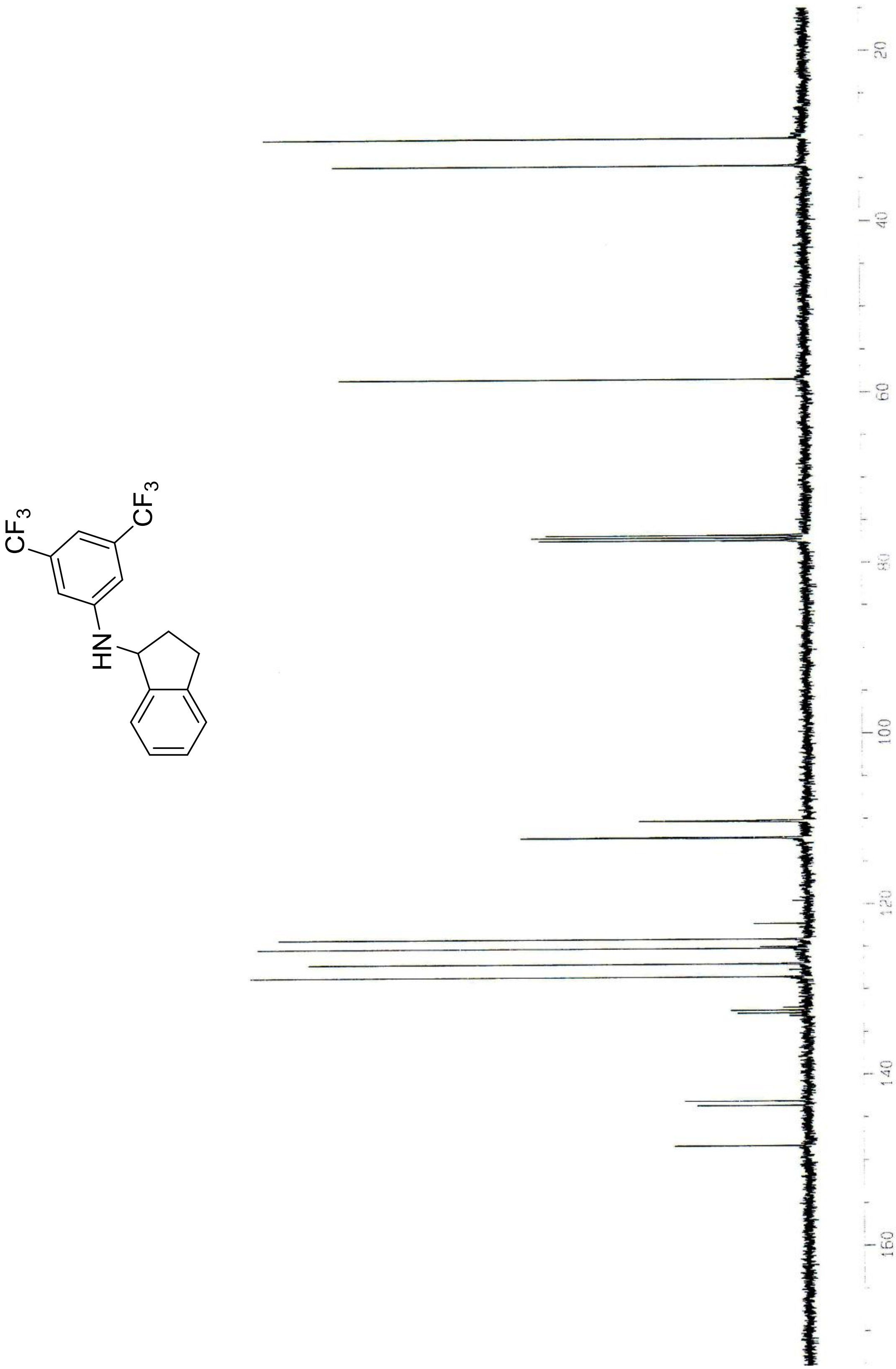
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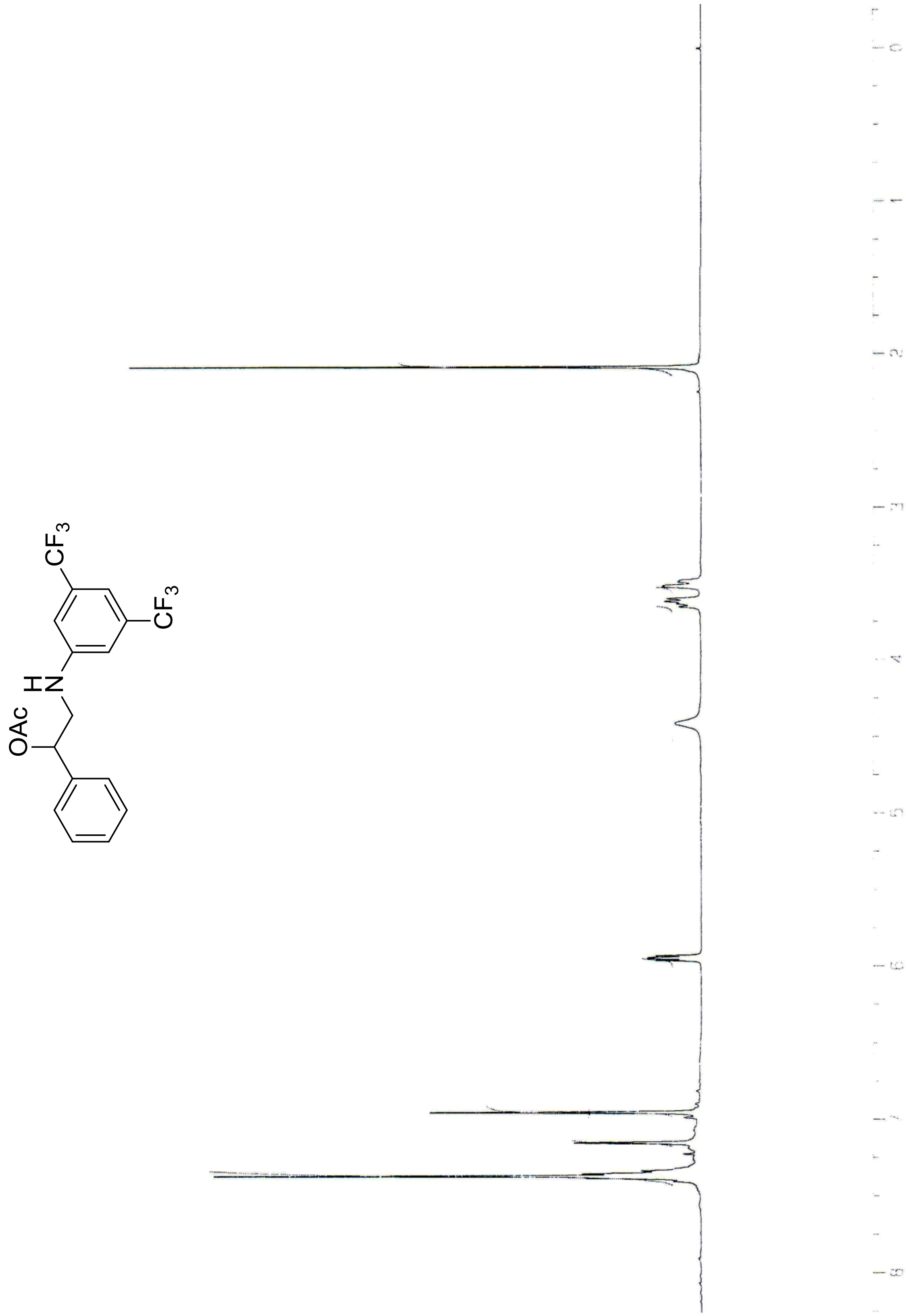
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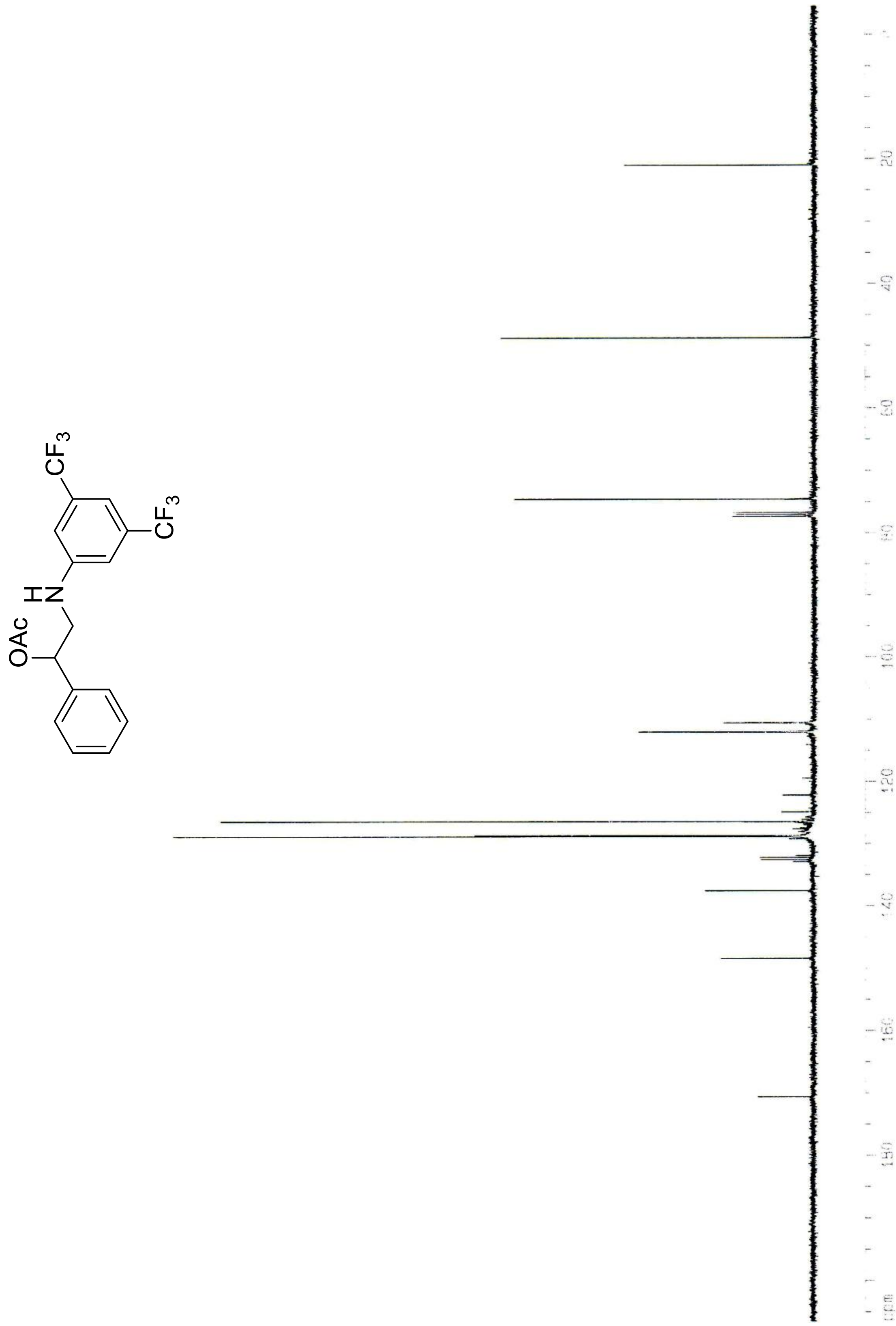
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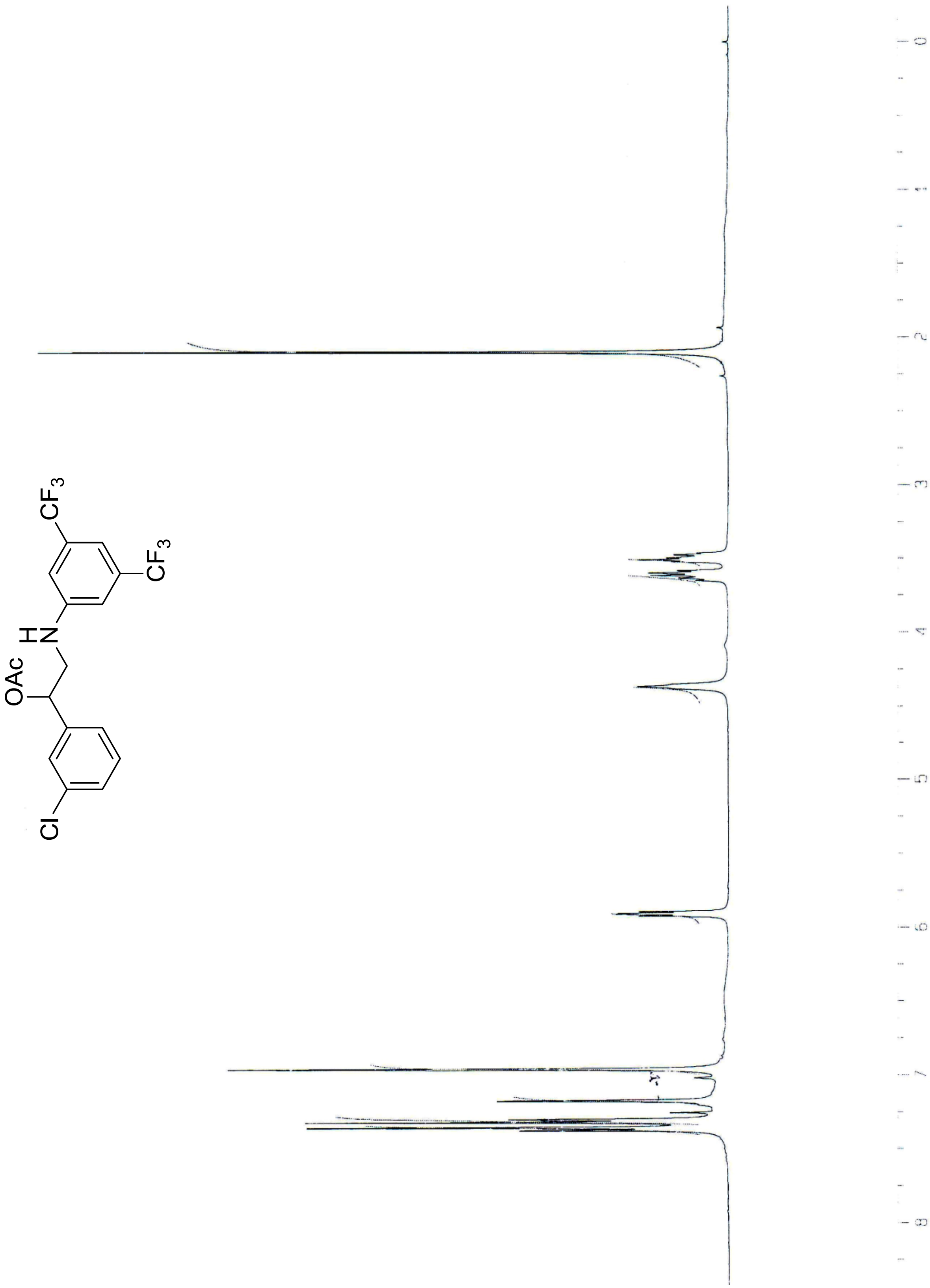
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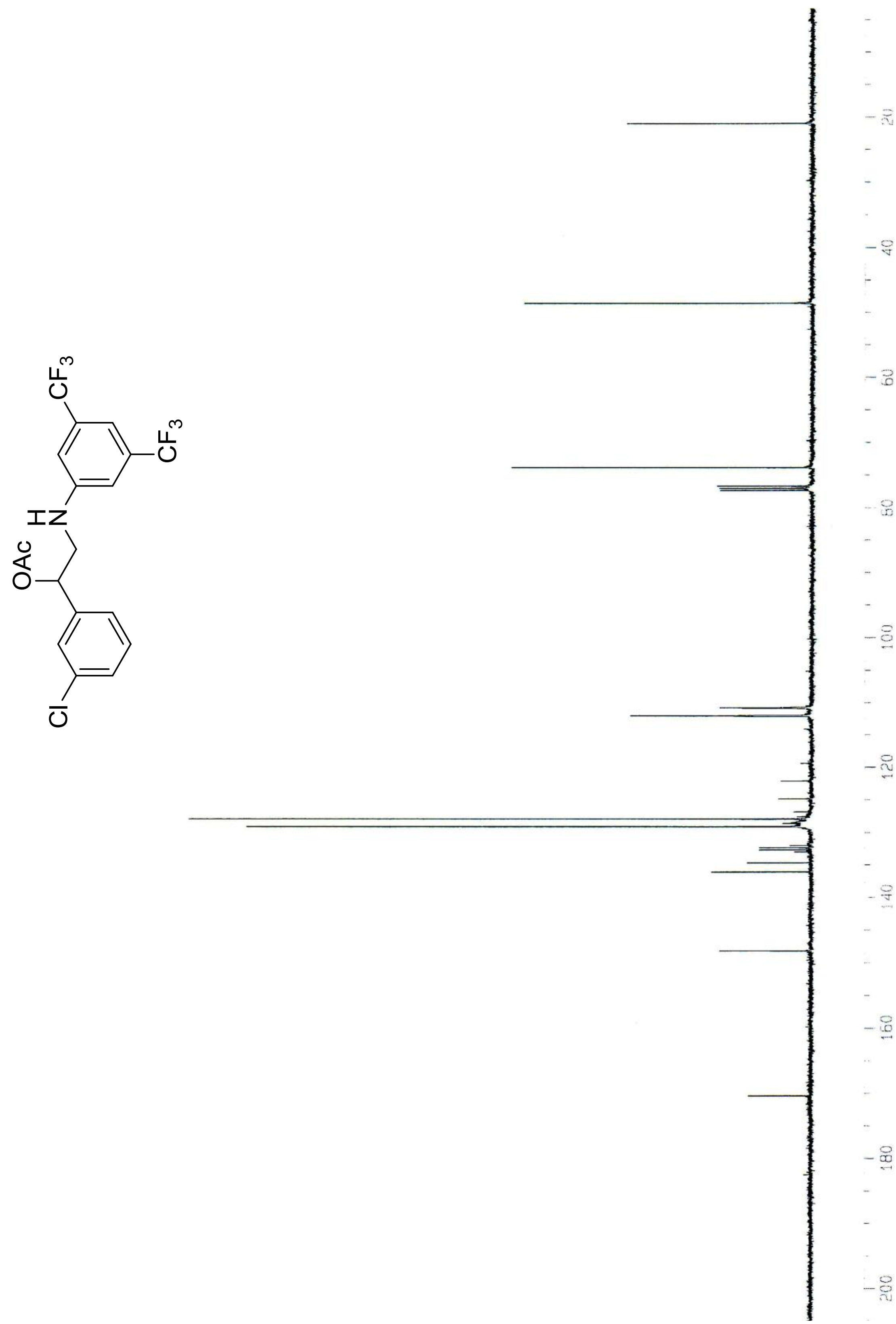

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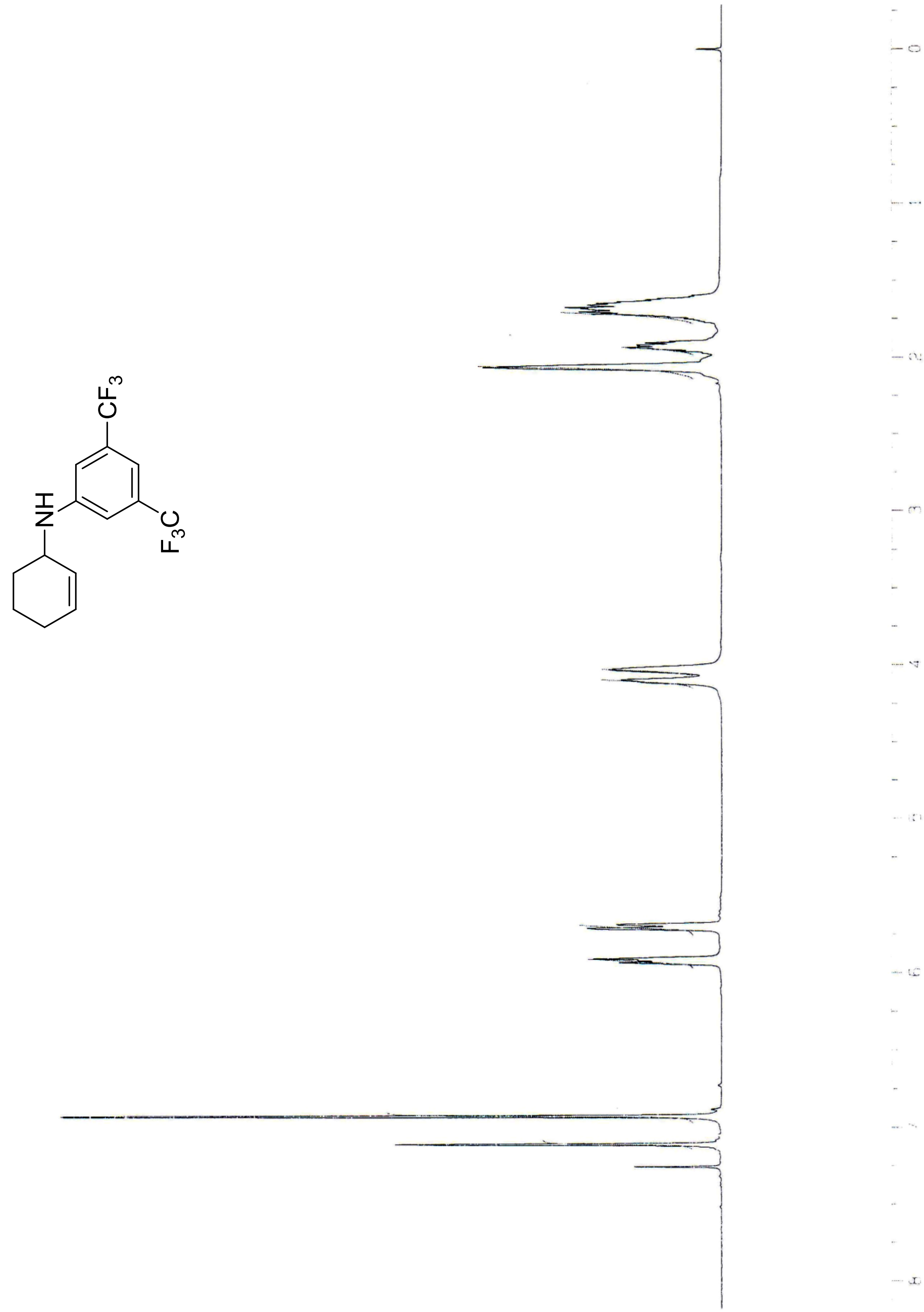
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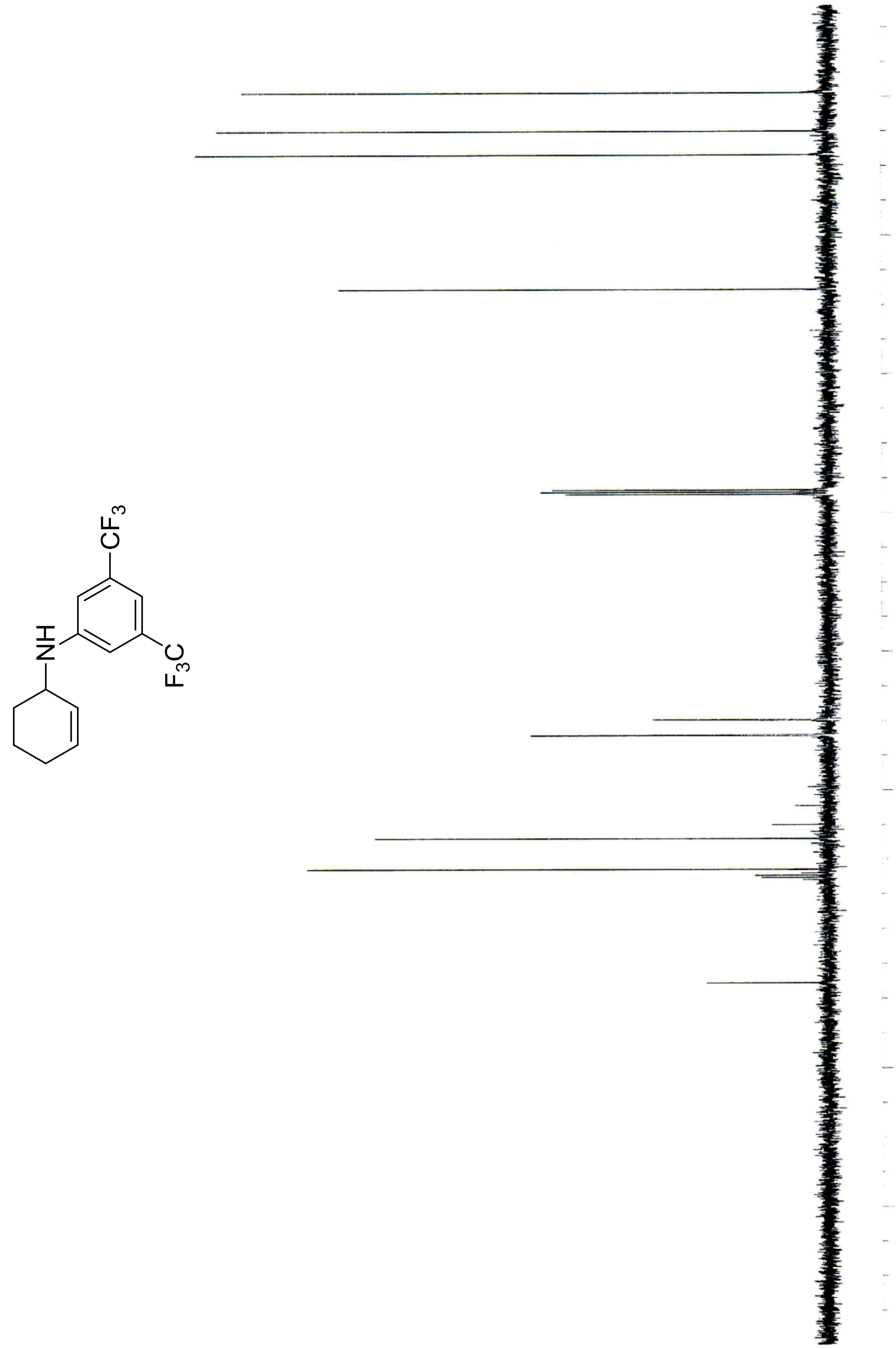
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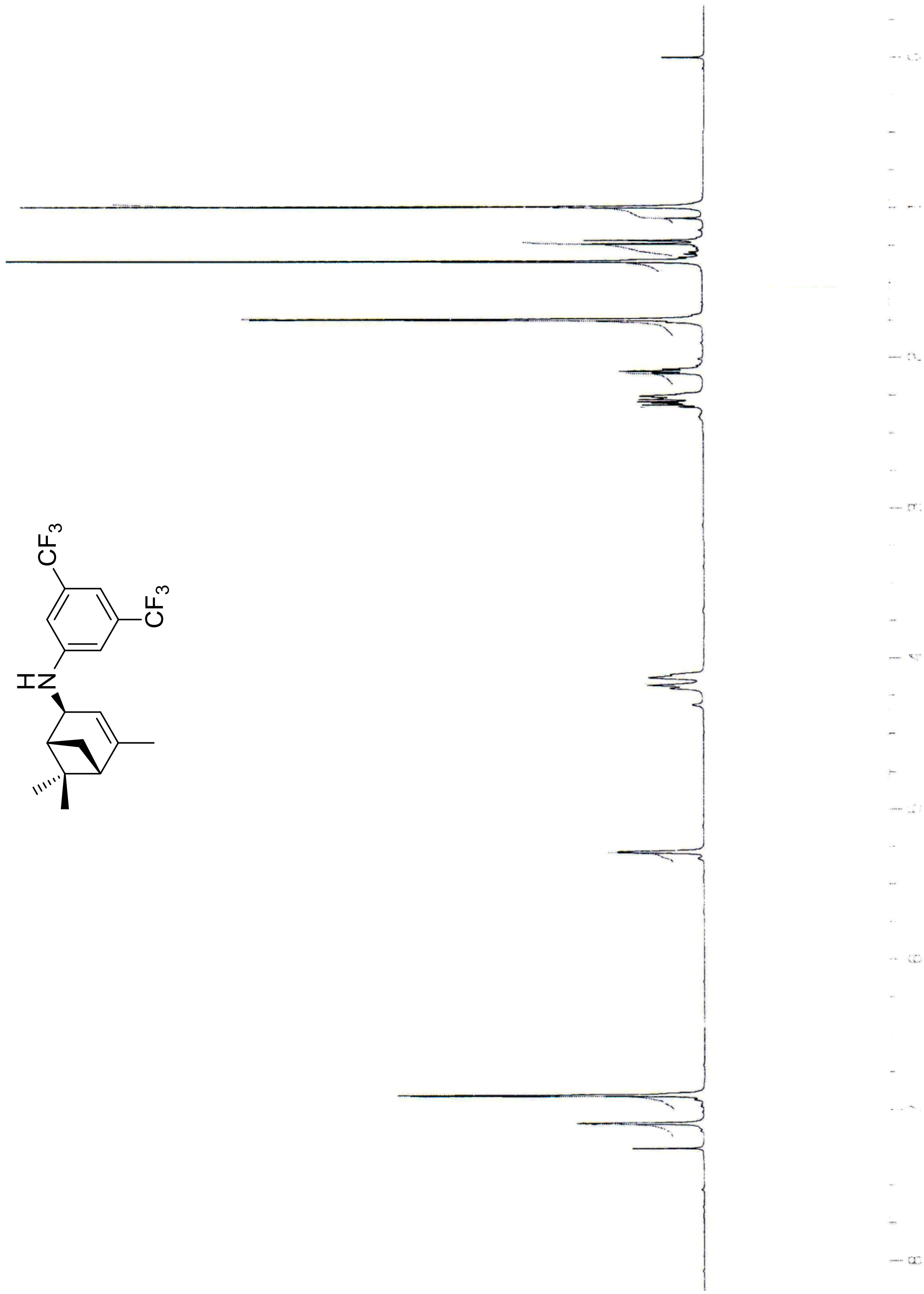
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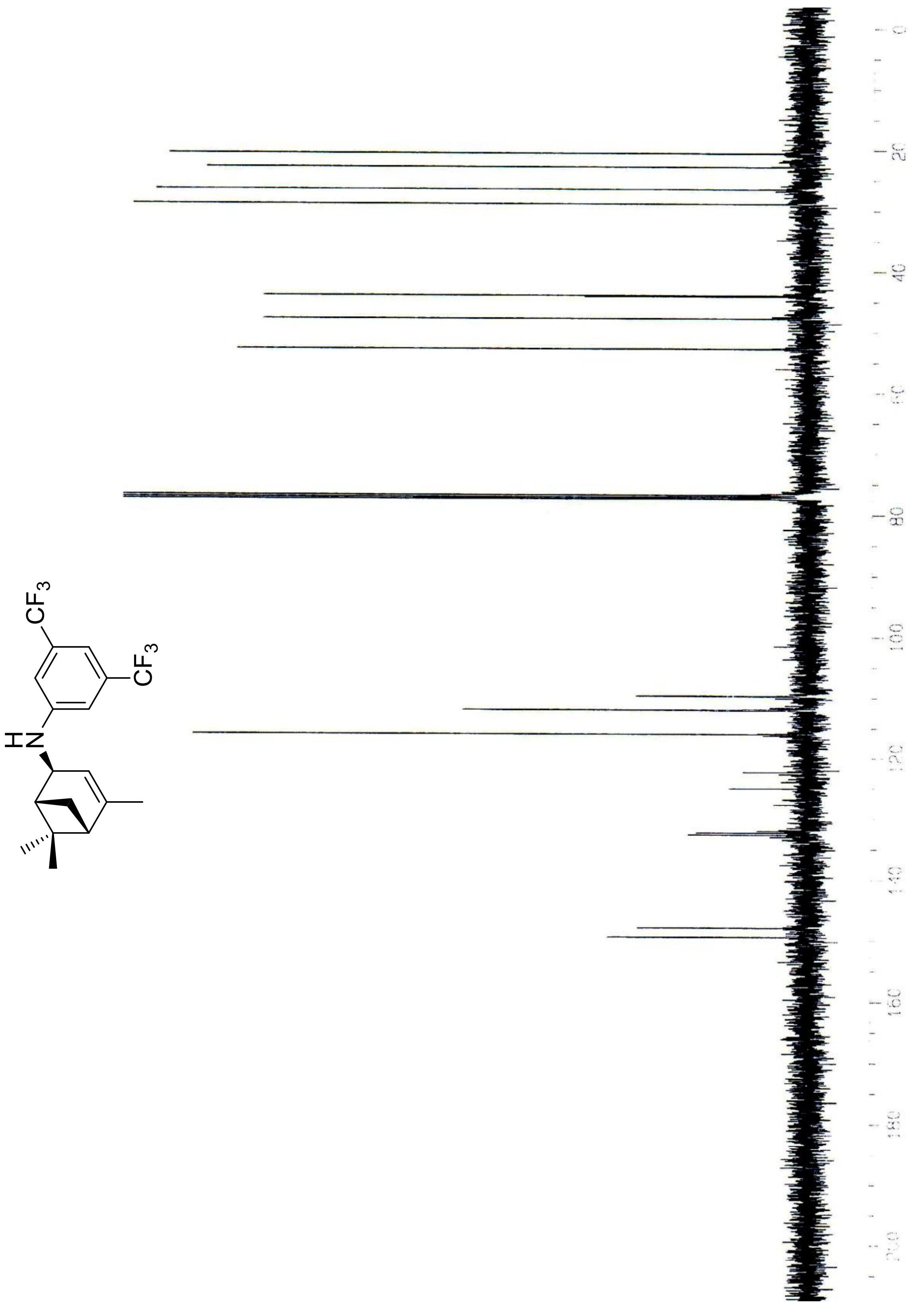
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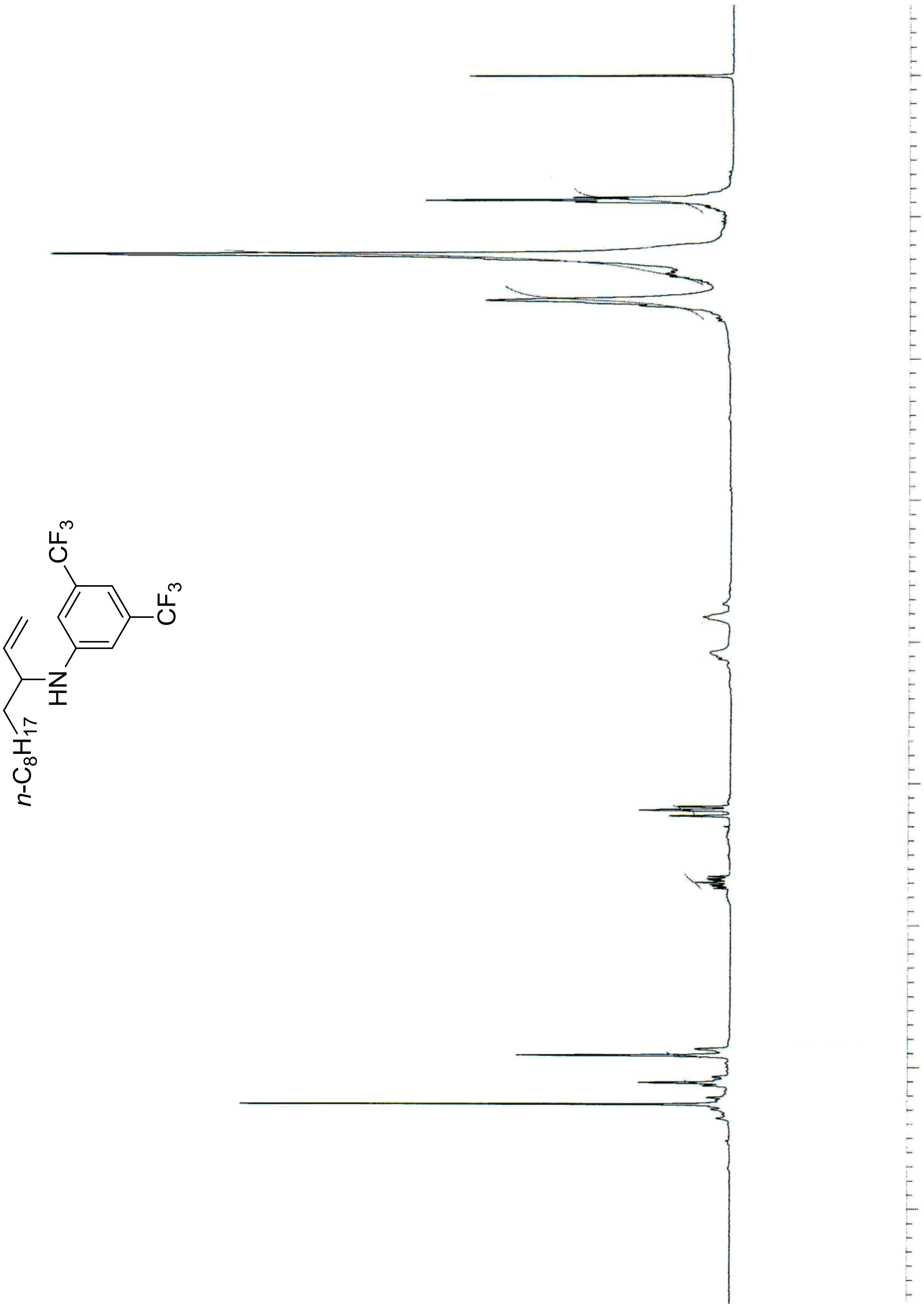
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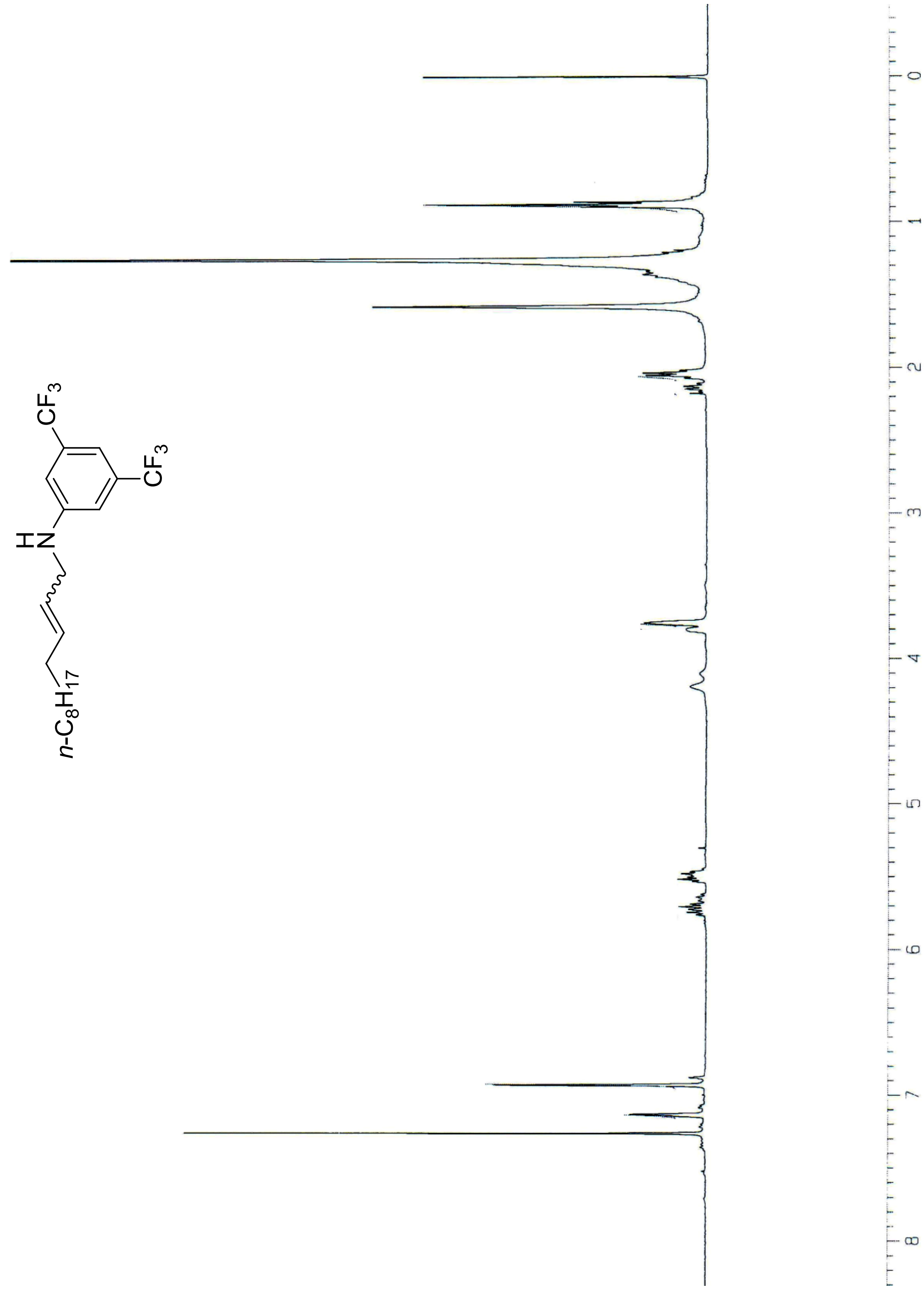
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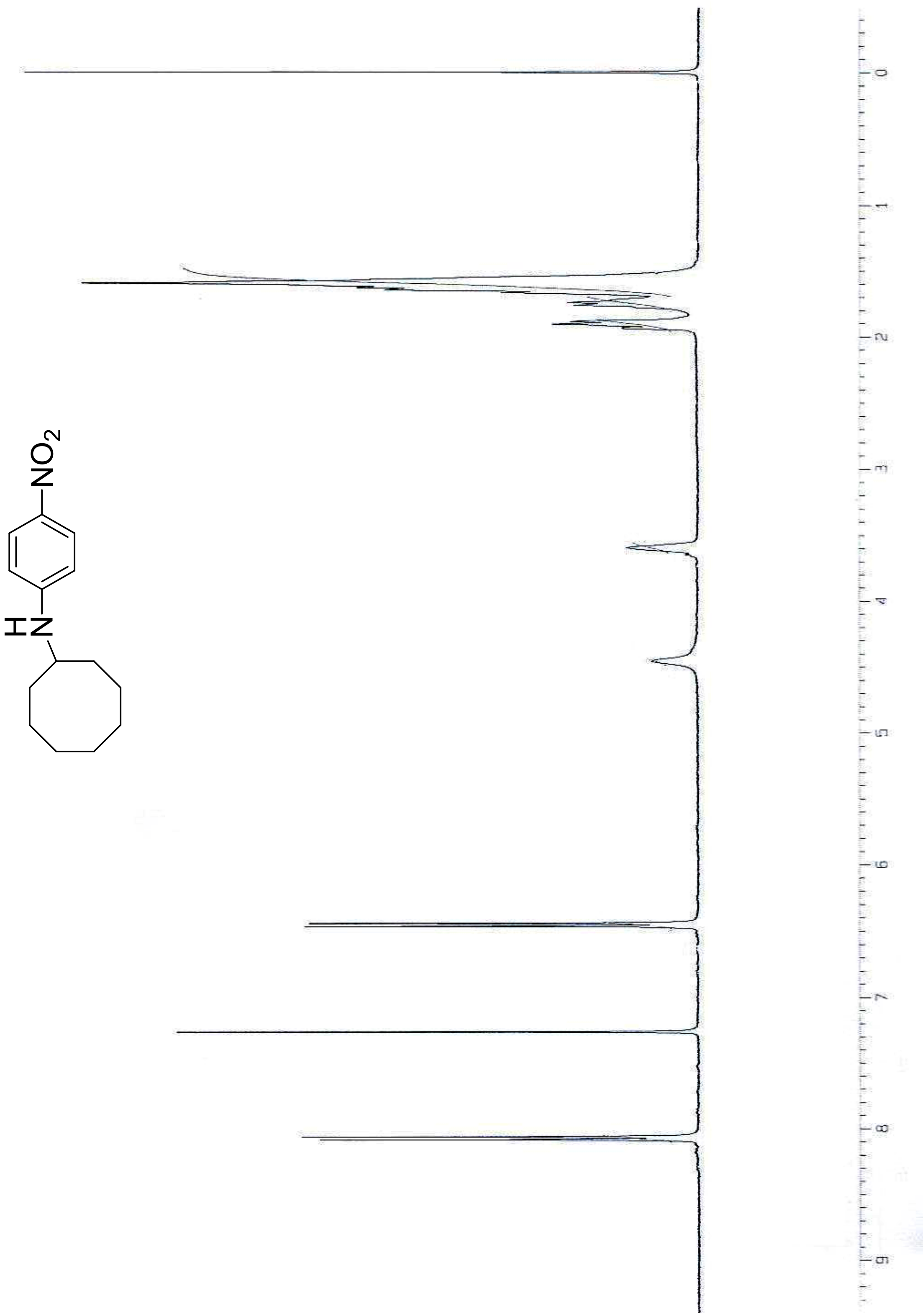
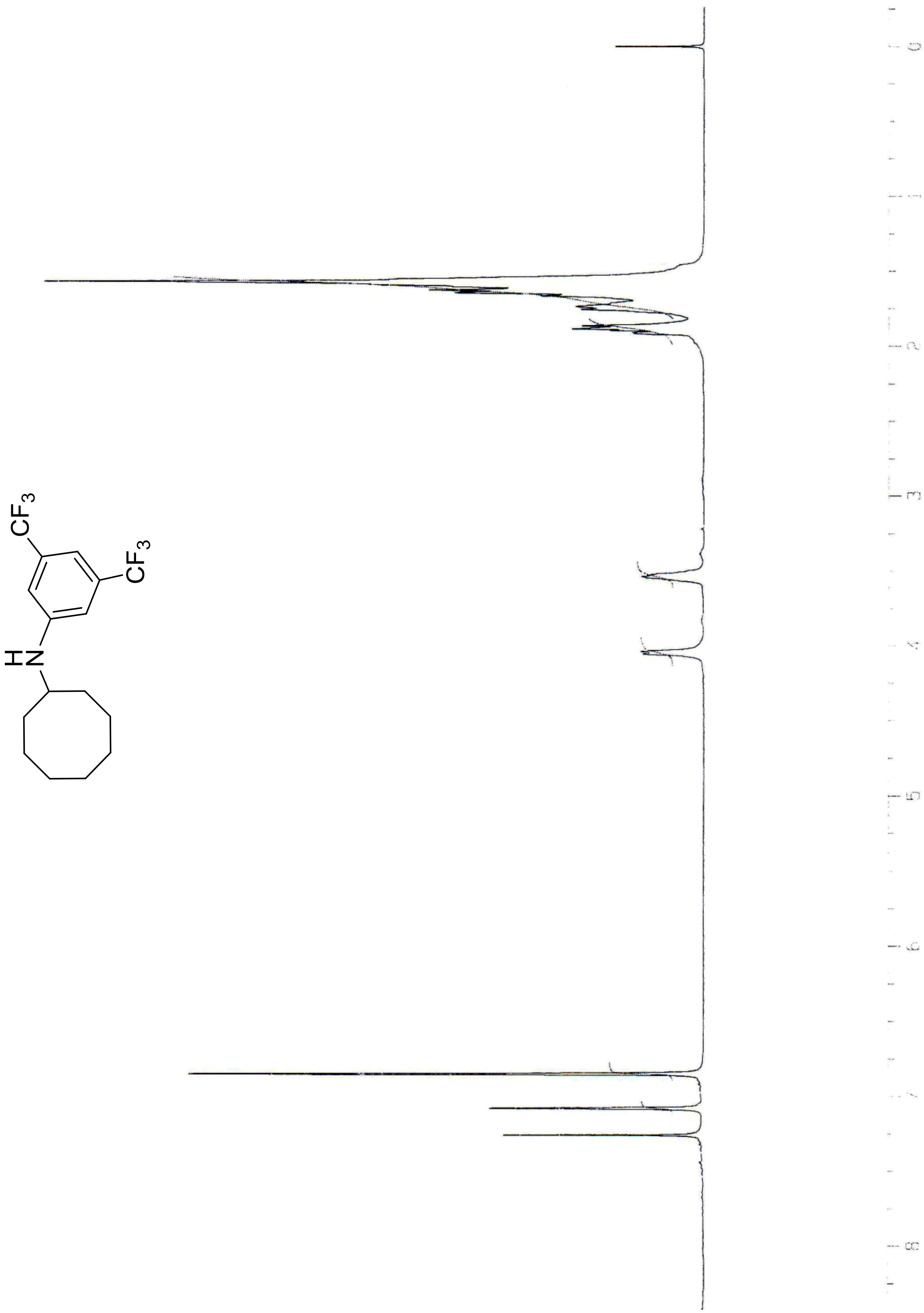
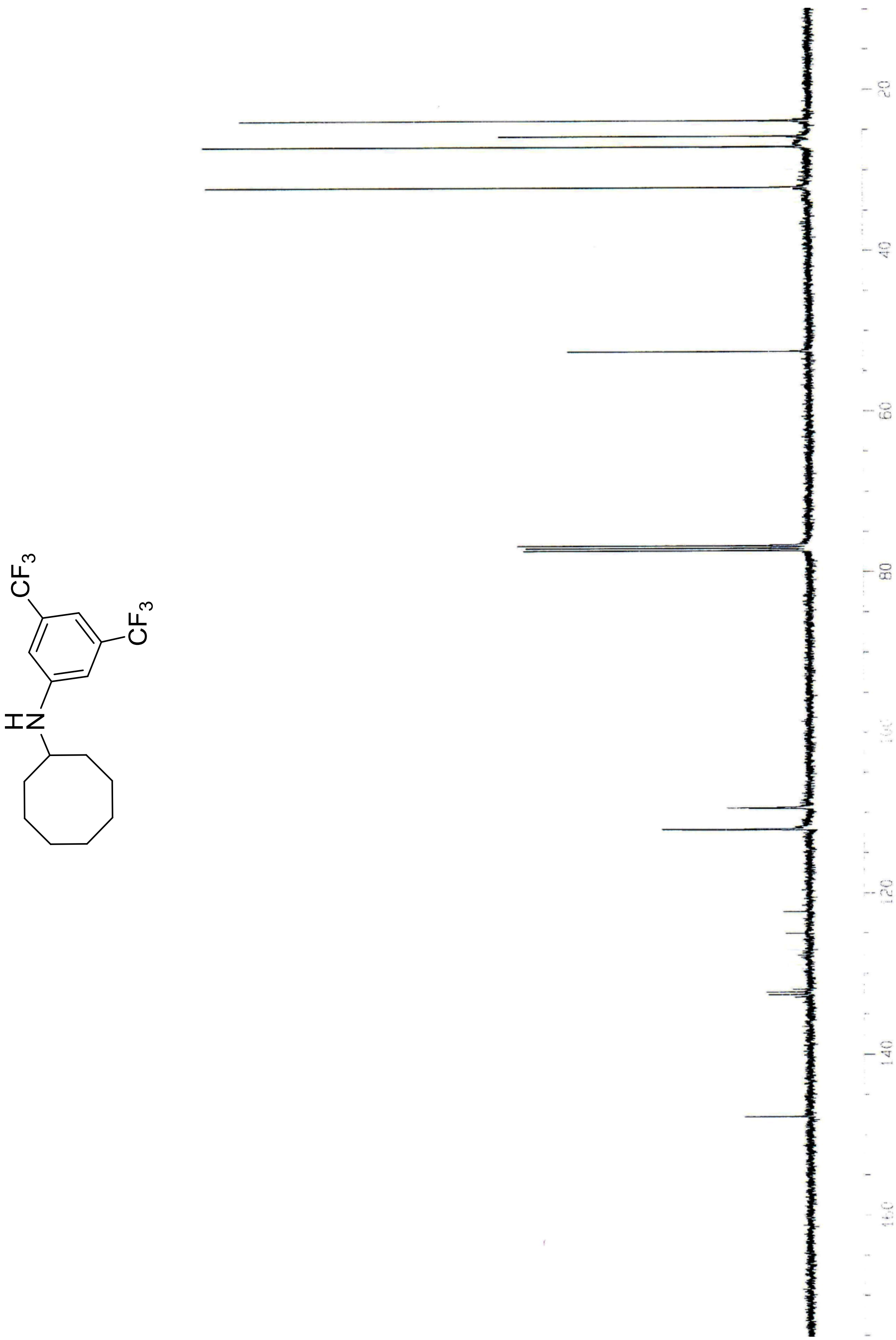
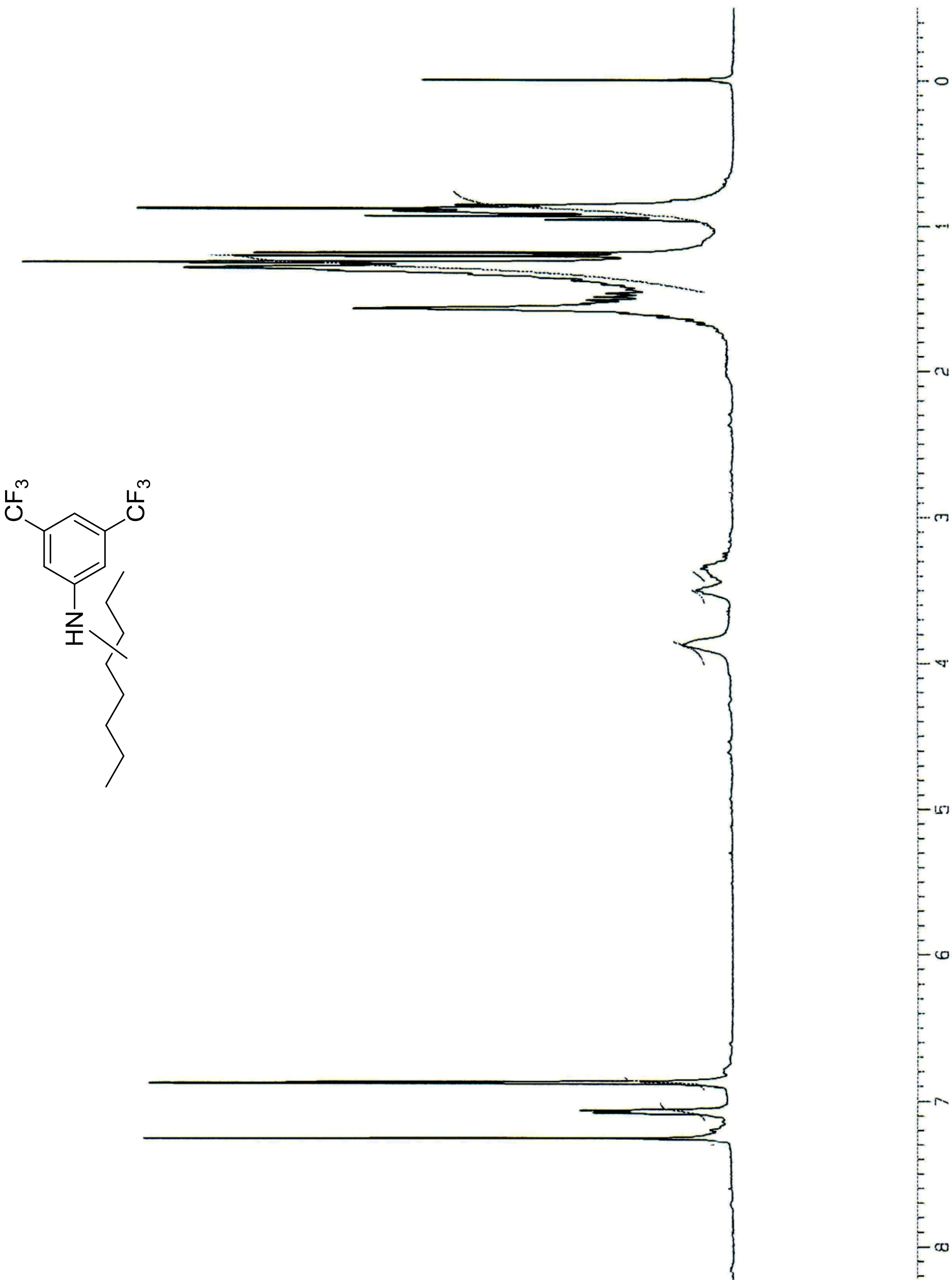


NO_2
HN


CF3
CF3
HN


CF3
CF3
H
N
20
40
60
80
120
140


CF3
CF3
HN
0
1
2
3
4
5
6
7
8