Enantioselective Chiral Pyridine-Catalyzed Carboxyl Migration Reactions for the Synthesis of Stereogenic Quaternary Carbons

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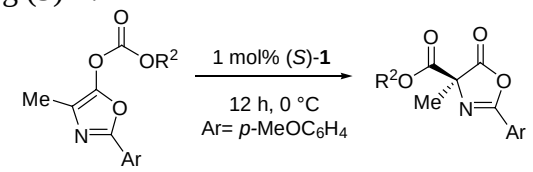
Table S-1. Steglich Rearrangment of **13a,b** using (*S*)-**1**.



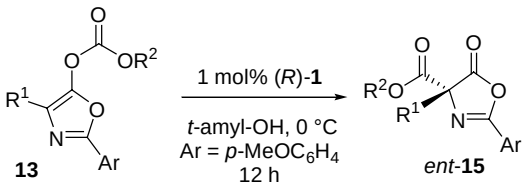
13a R^2 = Bn
13b R^2 = Ph
13c R^2 = Me

15

Entry	R^2	Solvent	Temp. (°C)	ee (%)[a]
1	Bn	CH_2Cl_2	23	30
2	Me[b]	CH_2Cl_2	23	30
3	Ph	CH_2Cl_2	0	73
4	Ph	THF	0	89
5	Ph	THF	-20	88
6	Ph	Et_2O	0	87
7	Ph	toluene	0	84
8	Ph	*t*-amyl-OH	0	91

(a) ee values were determined by hplc assay on chiral support (b) Ph in place of *p*-$MeOC_6H_4$

Table S-2. Scope of Steglich Rearrangement using (*R*)-**1**



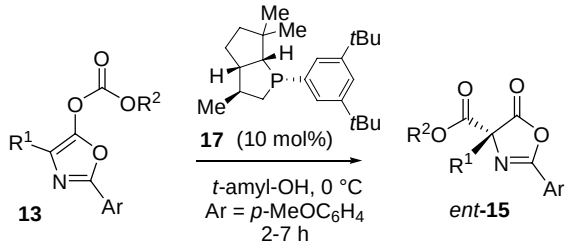
13

ent-**15**

Entry	Substrate	R^2	R^1	Yield (%)	ee (%)
1	**13b**	Ph	Me	95	91
2	**13d**	Ph	Bn	99	95

3	**13e**	Bn	Bn	NA	71
4	**13f**	Ph	allyl	90	91
5	**13g**	Ph	*i*Bu	90	91
6	**13h**	Ph	Ph	95	58

Table S-3. Rearrangement of **13** catalyzed by phosphine **17**



Entry	**Substrate**	**R^2**	**R^1**	**Yield (%)**	**ee (%)**
1	**13a**	Bn	Me	88	89
2[a]	**13a**	Bn	Me	87	85[a]
3[b]	**13a**	Bn	Me	73	92[b]
4	**13b**	Ph	Me	71	89
5	**13c**	Me	Me	90	88
6	**13e**	Bn	Bn	90	90
7	**13i**	Bn	allyl	91	90
8	**13j**	Bn	*i*Bu	87	92
9	**13k**	Bn	Ph	96	20

(a) Reaction at room temperature (b) reaction in 3:1 toluene: *t*-amyl-OH at -20 °C, 48 h.

Chemical Correlation of 15a and 15b. The chemical correlation was performed to define the configuration of **15b** (prepared from **13b** and the TADMAP catalyst (*S*)-**1**) using a procedure that converts *ent*-**15a** and **15b** into the same substituted amido-malonate diester **A** (below). This was done by ring opening of **15b** with benzyl alcohol under conditions of nucleophilic catalysis

in the presence of tributylphosphine/BzOH, resulting in selective activation of the azlactone carbonyl by the phosphine to afford diester **A** in 85% yield. A similar procedure was then applied to *ent*-**15a** and phenol, and gave the diester **A** in 70% yield with the same dominant configuration at the quaternary carbon. The enantiomeric excess of the starting materials was preserved in both processes as confirmed by analytical HPLC on chiral support (see experimental), a finding that rules out the interconversion of the azlactone and carboxylate carbonyl groups in the course of azlactone ring cleavage. The configuration of the TADMAP-derived **15b** could then be deduced, and the stereochemistry of the other *C*-carboxyl azlactones **15** and *ent*-**15** was assigned by analogy; see experimental, pages S-36 to S-37.

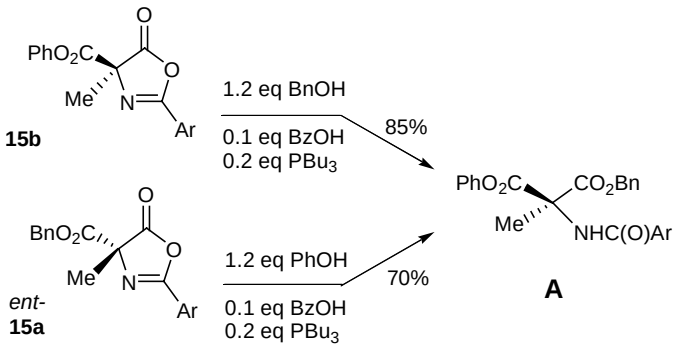
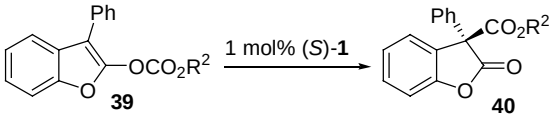


Table S-4. 3-Phenylbenzofuran enol carbonate rearrangements



Entry	Substrate	Solvent	Temp. (°C)	Time (h)	ee (%)
1	**39a**	CH_2Cl_2	23	1	2
2	**39b**	CH_2Cl_2	23	2	28
3	**39b**	THF	23	2	40
4	**39b**	THF	-20	12	52
5	**39b**	Et_2O	23	2	43
6	**39b**	Et_2O	-20	12	57
7	**39b**	toluene	23	2	44
8	**39b**	toluene	-20	12	59
9	**39b**	*t*-amyl-OH	23	2	26
10	**39c**	CH_2Cl_2	23	4	0
11	**39d**	CH_2Cl_2	23	2	51
12	**39d**	CH_2Cl_2	-20	12	72
13	**39d**	CH_2Cl_2	-40	18	86[a]
14	**39d**	THF	23	2	50
15	**39d**	THF	-20	12	67
16	**39d**	Et_2O	23	2	41
17	**39d**	Et_2O	-20	12	64
18	**39d**	toluene	23	2	46
19	**39d**	toluene	-20	12	54
20	**39e**	CH_2Cl_2	23	12	54
21	**39e**	THF	23	12	57
22	**39e**	Et_2O	23	12	45
23	**39e**	toluene	23	12	50

[a] 92% yield, 20 mol% **1** with 95% recovered

Experimental:

General Information

Et_2O, THF and CH_2Cl_2 were dried by passing them through a column of activated alumina. Toluene and Et_3N were distilled over CaH_2 prior to use. *t*-Amyl alcohol was carefully distilled over molten sodium. Organolithium reagents were titrated with diphenylacetic acid in THF prior to use. All other reagents were used as received from the manufacturer.

Analytical thin layer chromatography (tlc) was accomplished using Whatman 0.25 mm K6F Silica Gel 60 Å plates, and visualized with the aid of UV light or iodine vapor. Flash chromatography was accomplished according to the Still procedure[1] using Whatman Silica Gel: Puracil 60 Å (230-400 mesh).

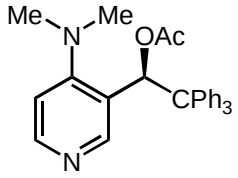
All reactions were performed under an atmosphere of nitrogen in oven-dried glassware.

Triphenylacetaldehyde 3. The known compound was prepared analogously to the precedented procedure.[2] To a slurry of $LiAlH_4$ (9.5 g, 250 mmol, Aldrich) at 0 °C in THF (425 mL) was added a solution of triphenylacetic acid (30 g, 104 mmol, Aldrich) in THF (250 mL) dropwise over approximately 30 min. The suspension was allowed to warm to rt and stirred for 24 h. The reaction was cooled to 0 °C and quenched by slow addition of 2 M HCl until the organic layer became clear. The reaction mixture was extracted with Et_2O, and the combined organics were washed with brine, dried over Na_2SO_4, filtered through Celite, and concentrated (aspirator) yielding triphenylethanol as a white crystalline solid (24.1 g, 85%). The product was sufficiently pure for the next step and was carried on without purification.

A solution of triphenylethanol (24.1 g, 88.0 mmol) in CH_2Cl_2 (176 mL) over activated 4 Å mol. sieves was treated with NMO (15.8 g, 135 mmol, Aldrich). The solution was cooled to 0

°C and treated with TPAP (80 mg, 0.220 mmol, Aldrich). Additional equal portions of TPAP were added once an hour for 3 h, then stirred for an additional 30 min and concentrated (aspirator). The residue was taken up in Et_2O and filtered through a plug of Celite and silica gel (2 cm/each) and concentrated (aspirator). The residue was purified by crystallization from Et_2O:hexanes yielding **3** as a yellow solid (18.0 g, 63% over two steps).

3-Bromo-4-dimethylaminopyridine 4. The known compound was prepared according to literature precedent,[3] but the chromatography step was replaced by filtration through a 4 cm silica gel plug with EtOAc as the eluent.



Acetic acid 1-(4-dimethylaminopyridin-3-yl)-2,2,2-triphenylethyl ester (1). To a solution of *t*BuLi in hexane (10.7 mL, 1.37 M, 14.6 mmol, Acros) at –78 °C was added a solution of 3-bromo-4-dimethylaminopyridine **4** (1.489 g, 7.405 mmol) in THF (67 mL) dropwise over 1 h. The resulting solution was added dropwise over 4 h to a solution of **3** (1.001 g, 3.676 mmol) in THF (50 mL) at –78 °C. The solution of crude lithium alkoxide was treated with acetic anhydride (3.5 mL, 37 mmol, Fluka) and allowed to warm to rt. The solution was poured into 2 M NaOH and extracted with CH_2Cl_2, and the combined organic layers were dried over $MgSO_4$, filtered and concentrated (aspirator) yielding an orange oil, which was purified by flash chromatography (silica gel; 5 x 15 cm column) using EtOAc eluent and collecting 20 mL fractions. Fractions 15-60 were combined to yield 931 mg (58%) of **1** as an off-white foam. HPLC (CHIRALCELL AD, 4.6mm x 25 cm, 90:10 hexane/isopropanol, 1.0 mL/min) T_R = 5.8 min ((*R*)-**1**), T_R = 8.1 min ((*S*)-**1**). Analytical tlc, EtOAc, Rf= 0.48. Molecular ion calculated for $C_{29}H_{29}N_2O_2$: 437.2224; [M+H], ESMS found m/z= 437.3; IR (neat, cm^{-1}) 1736, C=O; 1587,

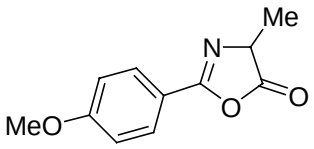
C=N; 1234, C-O; 500 MHz ^{1}H NMR ($CDCl_3$, ppm) δ 8.18 (1 H, d, J= 5.4 Hz) 7.69 (1 H, s) 7.40 (1 H, s) 7.28-7.17 (15 H, m) 6.71 (1 H, d, J= 5.4 Hz) 2.70 (6 H, s) 1.95 (3 H, s). ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 170.1, 159.3, 152.2, 149.5, 143.3, 130.7, 127.3, 126.5, 126.2, 114.0, 72.4, 64.2, 43.6, 21.3.

Procedure for the resolution of 1. *rac*-**1** (0.382 g, 0.875 mmol) and (+)-camphorsulfonic acid (CSA, 0.102 g, 0.439 mmol, Aldrich) were dissolved in warm toluene (95 mL) and allowed to cool and condense under a gentle stream of N_2. After approximately half the solvent had evaporated, a white crystalline solid precipitated and was filtered off. The crystals were washed with cold toluene, taken up in CH_2Cl_2, and the solution was extracted with 2 M NaOH, dried over $MgSO_4$, filtered and concentrated (aspirator) yielding **1** as a white crystalline solid (82 mg, 0.188 mmol, 86% ee). Repeating the process on the solid using (+)-CSA gave (*S*)-**1** (45 mg, 0.103 mmol, 12% overall yield, >99%ee). The original mother liquor was concentrated, the residue taken up in CH_2Cl_2, extracted with 2 M NaOH, dried over $MgSO_4$, filtered and concentrated (aspirator) yielding a **1** as a yellow solid (300 mg, 0.687 mmol, 27% ee). Repeating the crystallization procedure on this low ee material with (-)-CSA as the resolving agent allowed isolation of crystals that upon workup produced (*R*)-**1** (95 mg, 0.218 mmol, 25% overall yield, 96% ee) after a single crystallization. This procedure can be performed on 7.4 g scale yielding 0.7g of (*R*)-**1** (>99% ee, $[a]_D^{24}$= -90°), 1.0g of (*S*)-**1** (98.3% ee) and 4.7 g of low ee material that can be resubjected to the resolution.

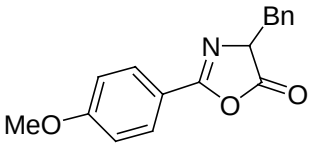
Determination of Absolute Stereochemistry of Catalyst 1. In a small glass vial, (+)-**1** (25 mg, 0.057 mmol) and dibenzoyl-(L)-tartaric acid (20 mg, 0.057 mmol, Aldrich) were dissolved in a minimal amount of EtOH (~0.5 mL). This vial was placed in a chamber containing hexane, and allowed to sit at room temperature until crystallization of **11** had occurred. These crystals were

examined by X-ray crystallography and given the known stereochemistry of the acid, the stereochemistry of (+)-**1** could be deduced as *S* according to the Cahn-Ingold-Prelog rules. See appendix for X-ray structure. Mp = 128 °C (melting with decomposition). Analytical tlc, 9:1 CH_2Cl_2/MeOH, Rf=0.50. Molecular ion calculated for $C_{29}H_{29}N_2O_2$: 437.2224; [M_1+H], ESMS found m/z= 437.2219; IR (neat, cm^{-1}) 1724, C=O; 1540, C=N; 1263, C-O; 500 MHz NMR ($CDCl_3$, ppm) δ 8.07 (1 H, d, J= 7.0 Hz) 8.01-7.99 (4 H, m) 7.70 (1 H, s) 7.47-7.43 (2 H, m) 7.34 (1 H, s) 7.32-7.23 (16 H, m) 7.10-7.08 (6 H, m) 6.56 (1 H, d, J= 7.0 Hz) 5.97 (2 H, s) 3.72 (2 H, q, J= 6.8 Hz) 2.96 (6 H, s) 2.09 (3 H, s) 1.24 (3 H, t, J= 6.8 Hz). ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 170.9, 170.8, 165.7, 160.0, 142.9, 142.2, 138.8, 133.2, 130.7, 130.2, 129.8, 128.4, 128.2, 127.8, 121.7, 110.7, 72.8, 70.4, 63.9, 58.7, 43.2, 21.5, 18.7.

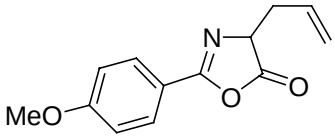
*Synthesis of Azlactones **12***



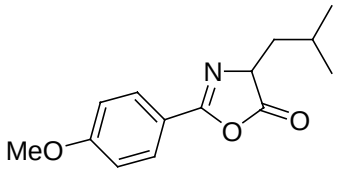
2-(4-Methoxyphenyl)-4-methyloxazolone. *N*-Anisoyl-alanine (1.0 g, 4.5 mmol), prepared according to literature precedent from alanine ethyl ester•HCl (Aldrich),[8] was mixed in a flask with acetic anhydride (2.7 mL, 28.4 mmol, Acros) and heated to 65 °C. After 30 min the solution was cooled and concentrated (aspirator). The residual acetic acid/anhydride was removed by dissolving the residue in toluene and concentration (aspirator, high vac) yielding azlactone as a white solid (0.836 g, 91%). The known compound was sufficiently pure for subsequent steps and no further purification was performed.



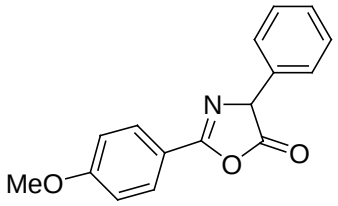
2-(4-Methoxyphenyl)-4-benzyloxazolone. *N*-Anisoyl-phenylalanine (1.0 g, 3.3 mmol), prepared according to literature precedent from phenylalanine methyl ester•HCl (Aldrich),[8] was mixed in a flask with acetic anhydride (2.0 mL, 21 mmol, Acros) and heated to 65 °C. After 30 min the solution was cooled and concentrated (aspirator). The residual acetic acid/anhydride was removed by dissolving the residue in toluene and concentration (aspirator, high vac) yielding azlactone as a white solid (0.917 g, 98%). The known compound was sufficiently pure for subsequent steps and no further purification was performed.



2-(4-Methoxyphenyl)-4-allyloxazolone. *N*-Anisoyl-2-amino-4-pentenoic acid (1.523 g, 6.11 mmol), prepared according to literature precedent from 2-amino-4-pentenoic acid (Aldrich),[8] was mixed in a flask with acetic anhydride (3.5 mL, 37 mmol, Acros) and heated to 65 °C. After 90 min the solution was cooled and concentrated (aspirator). The residual acetic acid/anhydride was removed by dissolving the residue in toluene and concentration (aspirator, high vac) yielding azlactone as a yellow solid (1.399 g, 99%). The known compound was sufficiently pure for subsequent steps and no further purification was performed.



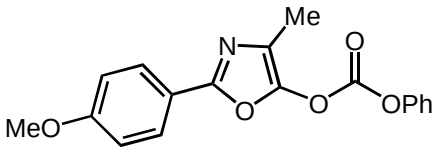
2-(4-Methoxyphenyl)-4-isobutyloxazolone. *N*-Anisoyl-leucine (1.535 g, 5.8 mmol), prepared according to literature precedent from leucine methyl ester•HCl (Aldrich),[8] was mixed in a flask with acetic anhydride (3.5 mL, 37 mmol, Acros) and heated to 65 °C. After 30 min the solution was cooled and concentrated (aspirator). The residual acetic acid/anhydride was removed by dissolving the residue in toluene and concentration (aspirator, high vac) yielding azlactone as a white solid (1.352 g, 94%). The known compound was sufficiently pure for subsequent steps and no further purification was performed.



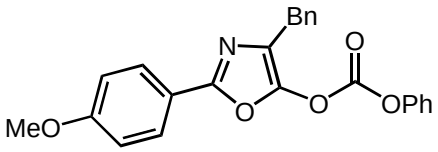
2-(4-Methoxyphenyl)-4-phenyloxazolone. The known compound *N*-anisoyl-phenylglycine (0.500 g, 1.75 mmol) in CH_2Cl_2 (3 mL), prepared analogously to literature precedent from phenylglycine methyl ester•HCl,[9] was mixed with a solution of DCC in CH_2Cl_2 (4 mL) at 0 °C. The resulting suspension was allowed to warm to rt and stir for 12 h. The slurry was filtered and the solid washed with CH_2Cl_2. The liquid was then concentrated (aspirator), taken up in Et_2O and filtered again. After removal of the solvent (aspirator) azlactone was isolated as a yellow crystalline solid (0.493 g, quantitative) The known compound was slightly contaminated with dicyclohexylurea but sufficiently pure for subsequent steps and no further purification was performed.

Azlactone Enol Carbonate Synthesis

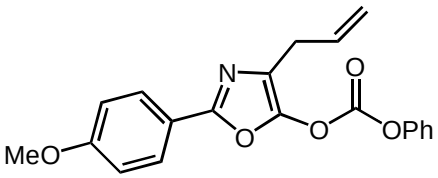
Enol carbonates **13a**, **13c**, **13e**, **13i**, and **13j** were prepared according to literature precedent.[8] The remaining unfunctionalized enol carbonates were prepared according to the general process described below for the synthesis of enol carbonate **13b**.



5-Phenoxycarboxyl-4-methyl-2-(4-methoxyphenyl)-oxazole (13b). Et_3N (0.15 mL, 1.08 mmol, Aldrich) was added to a solution of 2-(4-methoxyphenyl)-4-methyloxazolone (0.200 g, 0.975 mmol) in THF (3 mL) at 0 °C. Phenyl chloroformate (0.13 mL, 1.036 mmol, Aldrich) was added, causing a white precipitate to form. The mixture was allowed to stir at 0 °C for 30 min, then poured into H_2O, and extracted with Et_2O. The combined organic layers were washed with 0.1 M HCl, sat aq $NaHCO_3$, and brine, dried over $MgSO_4$, filtered and concentrated (aspirator). The residue was purified by flash chromatography on silica gel (1:1 Et_2O:hexane) yielding **13b** as a white crystalline solid (0.285 g, 90%). Analytical tlc, 1:1 hexane/Et_2O, Rf= 0.36. Molecular ion calculated for $C_{18}H_{15}NO_5$: 325.0950; [M^+], EIMS found m/z= 325.0943; IR (neat, cm^{-1}) 1801, C=O; 1499, C=N; 1215, C-O; 500 MHz NMR ($CDCl_3$, ppm) δ 7.90 (2 H, d, J= 8.8 Hz) 7.46-7.43 (2 H, m) 7.33-7.29 (3 H, m) 6.95 (2 H, d, J= 8.8 Hz) 3.85 (3 H, s) 2.19 (3 H, s). ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 161.3, 155.1, 150.7, 150.1, 145.3, 129.7, 127.6, 126.8, 120.5, 120.3, 119.8, 114.1, 55.3, 10.3.

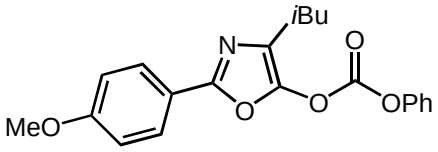


5-Phenoxycarboxyl-4-benzyl-2-(4-methoxyphenyl)-oxazole (13d). Et_3N (0.11 mL, 0.789 mmol, Aldrich) was added to a solution of 2-(4-methoxyphenyl)-4-benzyloxazolone (0.200 g, 0.711 mmol) in THF (3 mL) at 0 °C. Phenyl chloroformate (0.10 mL, 0.797 mmol, Aldrich) was added, causing a white precipitate to form. The mixture was allowed to stir at 0 °C for 2 h, then poured into H_2O, and extracted with Et_2O. The combined organic layers were washed with 0.1 M HCl, sat aq $NaHCO_3$, and brine, dried over $MgSO_4$, filtered and concentrated (aspirator). The residue was purified by flash chromatography on silica gel (30:70 Et_2O:hexane) yielding **13d** as a white crystalline solid (0.223 g, 78%). Analytical tlc, 70:30 hexane/Et_2O, Rf= 0.38. Molecular ion calculated for $C_{24}H_{19}NO_5$: 401.1263; [M^+], EIMS found m/z= 401.1274; IR (neat, cm^{-1}) 1797, C=O; 1496, C=N; 1208, C-O; 300 MHz NMR ($CDCl_3$, ppm) δ 7.92 (2 H, d, J= 8.8 Hz) 7.45-7.41 (2 H, m) 7.36-7.25 (7 H, m) 7.19 (2 H, d, J= 8.8 Hz) 6.95 (2 H, d, J= 8.8 Hz) 3.94 (2 H, s) 3.86 (3 H, s). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 161.6, 155.6, 150.8, 150.2, 145.8, 137.6, 129.9, 129.1, 128.7, 127.9, 127.0, 126.8, 123.5, 120.7, 114.3, 110.0, 55.6, 31.9.

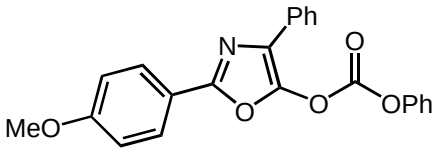


5-Phenoxycarboxyl-4-allyl-2-(4-methoxyphenyl)-oxazole (13f). Et_3N (0.16 mL, 1.15 mmol, Aldrich) was added to a solution of 2-(4-methoxyphenyl)-4-allyloxazolone (0.190 g, 0.769 mmol) in THF (3 mL) at 0 °C. Phenyl chloroformate (0.14 mL, 1.15 mmol, Aldrich) was added, causing a white precipitate to form. The mixture was allowed to stir at 0 °C for 2 h, then poured

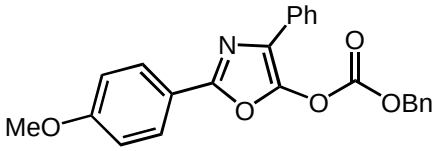
into H_2O, and extracted with Et_2O. The combined organic layers were washed with 0.1 M HCl, sat aq $NaHCO_3$, and brine, dried over $MgSO_4$, filtered and concentrated (aspirator) yielding **13f** as a yellow crystalline solid (0.266 g, 98%). Analytical tlc, 80:20:1 hexane/Et_2O/AcOH, Rf= 0.34. Molecular ion calculated for $C_{20}H_{17}NO_5$: 351.1107; [M^+], EIMS found m/z= 351.1100; IR (neat, cm^{-1}) 1799, C=O; 1500, C=N; 1213, C-O; 300 MHz NMR ($CDCl_3$, ppm) δ 7.93-7.90 (2 H, m) 7.47-7.42 (2 H, m) 7.34-7.26 (3 H, m) 6.96-6.93 (2 H, m) 6.08-5.95 (1 H, m) 5.27-5.16 (2 H, m) 3.86 (3 H, s) 3.35-3.33 (2 H, m). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 161.6, 155.6, 150.9, 150.4, 145.7, 133.7, 130.0, 127.9, 127.0, 127.0, 120.7, 120.0, 117.3, 114.3, 55.6, 29.9.



5-Phenoxycarboxyl-4-isobutyl-2-(4-methoxyphenyl)-oxazole (13g). Et_3N (0.26 mL, 1.90 mmol, Aldrich) was added to a solution of 2-(4-methoxyphenyl)-4-isobutyloxazolone (0.312 g, 1.26 mmol) in THF (5 mL) at 0 °C. Phenyl chloroformate (0.24 mL, 1.90 mmol, Aldrich) was added, causing a white precipitate to form. The mixture was allowed to stir at 0 °C for 2.5 h, then poured into H_2O, and extracted with Et_2O. The combined organic layers were washed with 0.1 M HCl, sat aq $NaHCO_3$, and brine, dried over $MgSO_4$, filtered and concentrated (aspirator) yielding **13g** as a clear oil (0.417 g, 90%). Analytical tlc, 80:20:1 hexane/Et_2O/AcOH, Rf= 0.37. Molecular ion calculated for $C_{21}H_{21}NO_5$: 367.1420; [M^+], EIMS found m/z= 367.1408; IR (neat, cm^{-1}) 1801, C=O; 1500, C=N; 1216, C-O; 400 MHz NMR ($CDCl_3$, ppm) δ 7.93-7.90 (2 H, m) 7.46-7.42 (2 H, m) 7.33-7.28 (3 H, m) 6.96-6.93 (2 H, m) 3.85 (3 H, s) 2.40 (2 H, d, J= 7.3 Hz) 2.14-2.04 (1 H, m) 0.99 (6 H, d, J= 7.3 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 161.5, 155.4, 150.9, 150.5, 145.9, 129.9, 127.9, 127.0, 123.9, 120.7, 120.2, 114.3, 55.6, 34.1, 27.8, 22.6.

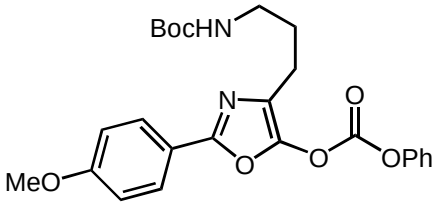


5-Phenoxycarboxyl-4-phenyl-2-(4-methoxyphenyl)-oxazole (13h). Et_3N (0.13 mL, 0.933 mmol, Aldrich) was added to a solution of 2-(4-methoxyphenyl)-4-phenyloxazolone (0.200 g, 0.748 mmol) in THF (3 mL) at 0 °C. Phenyl chloroformate (0.11 mL, 0.877 mmol, Aldrich) was added, causing a white precipitate to form. The mixture was allowed to stir at 0 °C for 30 min., then poured into H_2O, and extracted with Et_2O. The combined organic layers were washed with 0.1 M HCl, sat aq $NaHCO_3$, and brine, dried over $MgSO_4$, filtered and concentrated (aspirator). The residue was purified by flash chromatography on silica gel (1:2 Et_2O:hexane) yielding **13h** as a yellow crystalline solid (0.170 g, 59%). Analytical tlc, 1:1 hexane/Et_2O, Rf= 0.50. Molecular ion calculated for $C_{23}H_{17}NO_5$: 387.1107; [M^+], EIMS found m/z= 387.1103; IR (neat, cm^{-1}) 1795, C=O; 1501, C=N; 1236, C-O; 500 MHz NMR ($CDCl_3$, ppm) δ 8.02-8.00 (2 H, m) 7.88-7.86 (2 H, m) 7.48-7.41 (4 H, m) 7.36-7.28 (4 H, m) 6.99-6.97 (2 H, m) 3.87 (3 H, s). ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 161.8, 155.7, 151.0, 150.0, 144.9, 130.1, 130.0, 129.0, 128.2, 128.2, 127.2, 126.2, 123.8, 120.8, 119.9, 114.4, 55.7.



5-Benzyloxycarboxyl-4-phenyl-2-(4-methoxyphenyl)-oxazole (13k). Et_3N (0.28 mL, 2.01 mmol, Aldrich) was added to a solution of 2-(4-methoxyphenyl)-4-phenyloxazolone (0.500 g, 1.87 mmol) in THF (6 mL) at 0 °C. Benzyl chloroformate (0.27 mL, 1.90 mmol, Aldrich) was added, causing a white precipitate to form. The mixture was allowed to stir at 0 °C for 30 min., then poured into 5% aq HCl, and extracted with Et_2O. The combined organic layers were washed with 5% aq HCl, dried over $MgSO_4$, filtered and concentrated (aspirator). The residue was

purified by crystallization from hexane yielding **13k** as a white crystalline solid (0.575 g, 77%). Analytical tlc, 10:1:0.1 hexane/EtOAc/AcOH, Rf= 0.15. Molecular ion calculated for $C_{24}H_{20}NO_5$: 402.1336; [M+H], CIMS found m/z= 402.1335; IR (neat, cm^{-1}) 1783, C=O; 1501, C=N; 1168, C-O; 400 MHz NMR ($CDCl_3$, ppm) δ 7.99-7.95 (2 H, m) 7.78-7.76 (2 H, m) 7.44-7.37 (7 H, m) 7.32-7.27 (1 H, m) 6.98-6.94 (2 H, m) 5.34 (2 H, s) 3.85 (3 H, s). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 161.7, 155.5, 151.5, 145.1, 134.0, 130.1, 129.4, 129.0, 128.9, 128.8, 128.1, 128.0, 126.1, 123.5, 120.0, 114.4, 72.1, 55.6.



5-Phenoxycarboxyl-4-(3-*tert*-butoxycarbonylamino-propyl)-2-(4-methoxyphenyl)-oxazole (20b). *N*-Boc ornithine (0.232 g, 1.00 mmol, Sigma) was dissolved in a biphasic mixture of aqueous NaOH (0.29 mL, 3.5 M, 1.00 mmol, Fisher) and Et_2O (1 mL). The solution was cooled to 0 ºC and alternating portions of anisoyl chloride (0.171 g, 1.00 mmol, Aldrich) and aqueous NaOH (0.12 mL, 8.5 M, 1.00 mmol, Fisher) were added once ever 5 min for 30 min. The solution was allowed to stir overnight and warm to rt. The solution was acidified with conc. HCl and extracted with CH_2Cl_2. The combined organics were washed with brine, dried over $MgSO_4$, filtered and concentrated (aspirator) yielding α-amido acid **18** as a white, crystalline solid (0.343 g, 94%). The material was sufficiently pure for the next step and was carried on without additional purification.

The α-amido acid **18** (0.343 g, 0.936 mmol) was dissolved in CH_2Cl_2 (2 mL) and the resulting solution cooled to 0 ºC. To this solution was added a solution of DCC (0.193, 0.936 mmol, Aldrich) in CH_2Cl_2 (2.3 mL). The solution was allowed to warm to rt overnight, then

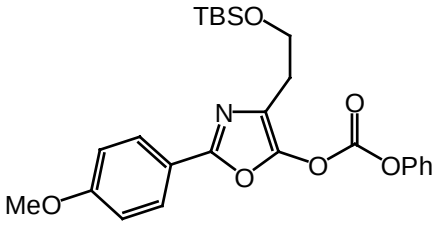
filtered and concentrated (aspirator) yielding the corresponding azlactone **19** as a clear oil. The material was carried on without purification.

Azlactone **19** (0.317 g, 0.910 mmol, estimated) was dissolved in THF (3 mL) and the resulting solution cooled to 0 ºC. To this solution was added Et_3N (0.14 mL, 1.004 mmol) and PhOCOCl (0.12 mL, 0.957 mmol, Aldrich) and a white precipitate formed immediately. The slurry was stirred at 0 ºC for 30 min, then poured into 0.1 M HCl, and extracted with Et_2O. The combined organics were washed with brine, dried over $MgSO_4$, filtered and concentrated (aspirator) and the residue purified by flash chromatography (silica, 3 x 15 cm) with 65:35 Et_2O/hexanes as the eluent yielding **20b** (0.333 g, 78% over two steps) as a clear, colorless oil. Analytical tlc, 65:35 ether/hexanes, Rf= 0.31. Molecular ion calculated for $C_{25}H_{28}N_2O_7$: 468.18960 [M+]; EIMS found m/z= 468.1882, error= 3 ppm; IR (neat, cm^{-1}) 1799, C=O; 1701, C=O; 1194, C-O; 300 MHz ^{1}H NMR ($CDCl_3$, ppm) δ 7.91 (2 H, d, J= 8.8 Hz) 7.46-7.43 (2 H, m) 7.33-7.30 (3 H, m) 6.95 (2 H, d, J= 8.8 Hz) 4.99 (1 H, br s) 3.86 (3 H, s) 3.22 (2 H, br q, J= 6.3 Hz) 2.57 (2 H, t, J= 7.3 Hz) 1.91 (2 H, p, J= 7.3 Hz) 1.44 (9 H, s). ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 161.7, 156.3, 151.0, 150.6, 145.4, 130.0, 127.9, 127.1, 123.8, 120.8, 120.0, 114.4, 79.2, 55.6, 40.2, 28.7, 28.2, 27.4.

5-Benzyloxycarboxyl-4-(3-*tert*-butoxycarbonylamino-propyl)-2-(4-methoxyphenyl)-oxazole (20a). Azlactone **19** was prepared as above.

Azlactone **19** (0.147 g, 0.420 mmol, used without purification following cyclization) was dissolved in THF (2 mL) and the resulting solution cooled to 0 ºC. To this solution was added Et_3N (0.070 mL, 0.504 mmol) and BnOCOCl (0.072 mL, 0.504 mmol, Aldrich) and a white precipitate formed immediately. The slurry was stirred at 0 ºC for 30 min, then poured into 0.1 M HCl, and extracted with Et_2O. The combined organics were washed with brine, dried over

$MgSO_4$, filtered and concentrated (aspirator) and the residue purified by flash chromatography (silica, 3 x 15 cm) with 12:1 EtOAc/hexanes as the eluent yielding **20a** (0.151 g, 75%) as a clear, colorless oil. The compound was sufficiently pure for subsequent steps and no further purification was performed.

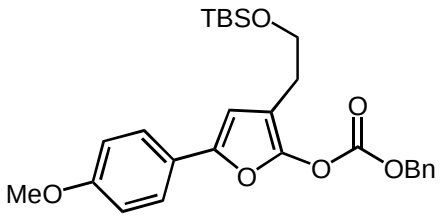


5-Phenoxycarboxyl-4-[2-(*tert*-butyldimethylsilanyloxy)-ethyl]-2-(4-methoxyphenyl)-oxazole (27b). The known[10] protected homoserine methyl ester **24** (2.0 g, 8.08 mmol) was dissolved in CH_2Cl_2 (38 mL). The solution was cooled to 0 ºC and treated with triethylamine (2.3 mL, 16.5 mmol, Aldrich) and anisoylchloride (1.4 g, 8.1 mmol, Aldrich). This solution was allowed to warm to room temperature and stir overnight. The solution was then extracted from 0.1 M HCl with CH_2Cl_2. The combined organics were dried over $MgSO_4$, filtered and concentrated (aspirator). The residue was purified by flash chromatography (1:1 Et_2O/hexanes) yielding the desired amido ester as a clear, colorless oil (2.3 g, 73% yield).

The resulting amido ester (0.300 g, 0.786 mmol) was dissolved in MeOH (1.5 mL). The solution was cooled to 0 ºC and treated with 2 M NaOH (0.40 mL, 0.800 mmol, Fisher) and stirred for 30 min at 0 ºC. The solution was then warmed to room temperature and concentrated (N_2 stream, vacuo). The residue was taken up in H_2O and extracted with Et_2O. The aqueous layer was poured into CH_2Cl_2 and the pH of the solution adjusted to pH = 2 by addition of 0.1 M HCl. The organic layer was dried over $MgSO_4$, filtered and concentrated (aspirator) yielding amido acid **25** (0.200 g, 69% yield) as a colorless wax. In order to avoid decomposition this compound was carried on without further purification.

Amido acid **25** (0.130 g, 0.353 mmol) was dissolved in CH_2Cl_2 (2 mL) and the solution was cooled to 0 ºC. To this solution was added DCC (72 mg, 0.353 mmol) and the solution was stirred at 0 ºC for 2 h. The solution was then filtered and concentrated (aspirator) and the residue taken up in Et_2O, filtered and concentrated (aspirator) yielding azlactone 12C as a clear, colorless oil. This compound was carried on without purification.

Azlactone **26** (used crude, 0.353 mmol estimated) was dissolved in THF (2 mL) and the solution was cooled to 0 ºC. The solution was treated with triethylamine (0.05 mL, 0.358 mmol, Aldrich) and phenyl chloroformate (0.044 mL, 0.351 mmol). The solution was stirred at 0 ºC for 30 min then extracted from 0.1 M HCl with Et_2O. The combined organics were washed with brine, dried over $MgSO_4$, filtered and concentrated (aspirator). The residue was purified via flash chromatography (75/23/2 hexanes:Et_2O:AcOH) yielding the enol carbonate **27b** as a clear, colorless oil (0.157 g, 95% yield from **25**). Analytical tlc, 75:23:2 hexane/ether/AcOH, Rf= 0.30. Molecular ion calculated for $C_{25}H_{31}NO_6Si$: 469.1920 [M^+]; EIMS found m/z= 469.1939; IR (neat, cm^{-1}) 1798, C=O; 1499, C=N; 1169, C-O; 300 MHz ^{1}H NMR ($CDCl_3$, ppm) δ 7.87 (2 H, d, J= 8.7 Hz) 7.42-7.38 (2 H, m) 7.29-7.25 (3 H, m) 6.91 (2 H, d, J= 8.7 Hz) 3.90 (2 H, t, J= 6.8 Hz) 3.81 (3 H, s) 2.73 (2 H, t, J= 6.8 Hz) 0.85 (9 H, s) 0.01 (6 H, s). ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 161.3, 155.2, 150.7, 150.1, 146.1, 129.7, 127.6, 126.7, 121.5, 120.5, 119.8, 114.1, 61.3, 55.3, 28.8, 25.9, 18.3.



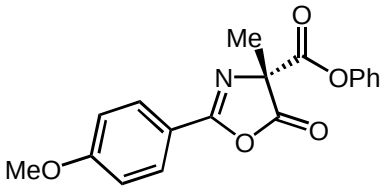
5-Benzyloxycarboxyl-4-[2-(*tert*-butyldimethylsilanyloxy)-ethyl]-2-(4-methoxyphenyl)-oxazole (27a). Azlactone **26** was prepared as above. Azlactone **26** (0.776 g crude material) was

dissolved in THF (16 mL) and the resulting solution cooled to 0 ºC. To this solution was added Et_3N (0.37 mL, 2.655 mmol) and benzyl chloroformate (0.38 mL, 2.63 mmol, Aldrich) with concominant formation of a white precipitate. The slurry was stirred at 0 ºC for 30 min, then poured into a solution of 0.1 M HCl, and extracted with Et_2O. The combined organics were washed with brine, dried over $MgSO_4$, filtered and concentrated (aspirator). The resulting residue was purified by flash chromatography (silica, 3 x 15 cm) with 83/16/1 hexanes/Et_2O/AcOH as the eluent yielding azlactone enol carbonate **27a** (0.443 g, 53%) as a clear, colorless oil. Analytical tlc, 70:30 hexane/ether, Rf= 0.45. Molecular ion calculated for $C_{26}H_{34}NO_6Si$: 484.21550 [M+H]; CIMS found m/z= 484.2149, error= 1 ppm; IR (neat, cm^{-1}) 1784, C=O; 1500, C=N; 1210, C-O; 300 MHz ^{1}H NMR ($CDCl_3$, ppm) δ 7.89-7.85 (2 H, m) 7.46-7.36 (5 H, m) 6.96-6.91 (2 H, m) 5.31 (2 H, s) 3.91-3.86 (5 H, m) 2.7 (2 H, t, J= 8.0 Hz) 0.87 (9 H, s) 0.02 (6 H, s). ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 161.5, 155.3, 151.9, 146.6, 134.1, 129.4, 129.0, 128.9, 127.8, 121.6, 120.2, 114.4, 71.9, 61.6, 55.6, 29.0, 26.1, 18.6, -5.1.

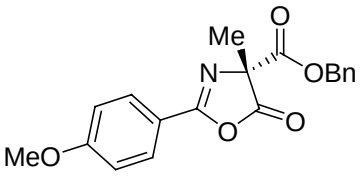
Azlactone Enol carbonate Carboxyl Migration

Procedure A - *General procedure for pyridine **1** catalyzed carboxyl migration of azlactone enol carbonates:* To a solution of azlactone enol carbonate **13** (0.100 mmol) in *t*-amyl alcohol (1.5 mL, Acros) at 0 °C was added (*R*)-**1** (0.44 mg, 0.001 mol, >99% ee) as a solution in *t*-amyl alcohol (0.5 mL, Acros). The solution was allowed to stand at 0 °C for 12 h, then quenched with iodomethane (0.1 mL, Acros) warmed to rt, and concentrated (aspirator). The residue was taken up in EtOAc and filtered through a 2 cm silica plug with EtOAc as the eluent. The solution was concentrated (aspirator) yielding >95% pure material by NMR assay unless noted.

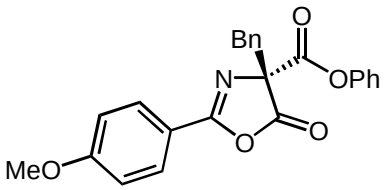
Procedure B - *General procedure for phosphine* **17** *catalyzed carboxyl migration of azlactone enol carbonates:* To a solution of azlactone enol carbonate **13** (0.100 mmol) in *t*-amyl alcohol (1.0 mL, Acros) at 0 °C, under N_2 was added **17**[11] (0.010 mmol, >99% ee) as a solution in *t*-amyl alcohol (1.0 mL, Acros). The solution was allowed to stand at 0 °C for 12 h, then quenched with iodomethane (0.1 mL, Acros) warmed to rt, and concentrated (aspirator). The residue was purified by flash chromatography (silica gel, 80:20:0.2 hexane/EtOAc/AcOH) yielding >95% pure material by NMR assay unless noted.



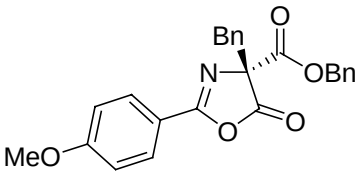
4-Methyl-5-oxo-2-(4-methoxyphenyl)-4,5-dihydrooxazole-4-carboxylic acid phenyl ester (15b). Starting with **13b**, procedure A was followed yielding **15b** as a clear, colorless oil (31 mg, 95%, 91% ee).[12] HPLC (Chiralpak AD, 4.6mm x 25 cm, 90:10 hexane/isopropanol, 1.0 mL/min) T_R = 8.0 min (minor), T_R = 9.5 min (major). Analytical tlc, 1:1 hexane/Et_2O, Rf= 0.40. Molecular ion calculated for $C_{18}H_{15}NO_5$: 325.0950; [M^+], EIMS found m/z= 325.0953; IR (neat, cm^{-1}) 1768, C=O; 1646, C=O; 1513, C=N; 500 MHz NMR ($CDCl_3$, ppm) δ 8.02 (2 H, d, J= 8.8 Hz) 7.38-7.35 (2 H, m) 7.26-7.23 (1 H, m) 7.10 (2 H, d, J= 8.8 Hz) 7.01 (2 H, d, J= 8.8 Hz) 3.90 (3 H, s) 1.87 (3 H, s). ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 175.0, 164.8, 163.8, 163.3, 150.2, 130.3, 129.5, 126.5, 121.1, 117.3, 114.3, 72.8, 55.6, 20.5.



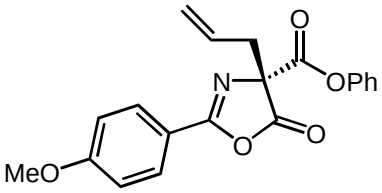
4-Methyl-5-oxo-2-(4-methoxyphenyl)-4,5-dihydrooxazole-4-carboxylic acid benzyl ester (15a). Starting with **13a**, procedure B was followed yielding the known compound **15a**[8] as a clear, colorless oil (30.1 mg, 88%, 89% ee). HPLC (Chiralcel OD, 4.6mm x 25 cm, 90:10:0.1 hexane/isopropanol/AcOH, 1.0 mL/min) T_R = 8.3 min (major), T_R = 10.2 min (minor).



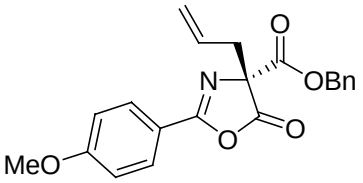
4-Benzyl-5-oxo-2-(4-methoxyphenyl)-4,5-dihydrooxazole-4-carboxylic acid phenyl ester (15d). Starting with **13d**, procedure A was followed yielding **15d** as a clear, colorless oil (40 mg, 99%, 95% ee). HPLC (Regis Whelk-O, 4.6mm x 25 cm, 90:10:0.1 hexane/isopropanol/AcOH, 1.0 mL/min) T_R = 11.5 min (minor), T_R = 13.5 min (major). Analytical tlc, mL, 75:25:0.1 hexane/Et_2O/AcOH, Rf= 0.40. Molecular ion calculated for $C_{24}H_{19}NO_5$: 401.1263; [M^+], EIMS found m/z= 401.1263; IR (neat, cm^{-1}) 1820, C=O; 1776, C=O; 1513, C=N; 500 MHz NMR ($CDCl_3$, ppm) δ 7.89 (2 H, d, J= 8.8 Hz) 7.41-7.38 (2 H, m) 7.29-7.19 (6 H, m) 7.12 (2 H, d, J= 7.8 Hz) 6.95 (2 H, d, J= 8.8 Hz) 3.87 (3 H, s) 3.74 (1 H, d, J= 13.7 Hz) 3.61 (1 H, d, J= 13.7 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 173.6, 164.5, 163.6, 163.1, 150.3, 132.8, 130.4, 130.2, 129.5, 128.3, 127.6, 126.5, 121.1, 117.2, 114.2, 77.5, 55.5, 40.2.



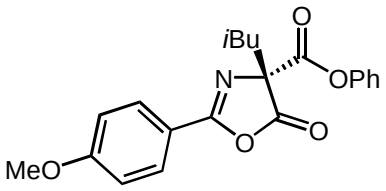
4-Benzyl-5-oxo-2-(4-methoxyphenyl)-4,5-dihydrooxazole-4-carboxylic acid benzyl ester (15e). Starting with **13e**, procedure B was followed yielding the known compound **15e** [8] as a clear, colorless oil (37 mg, 90%, 90% ee). HPLC (Regis Whelk-O, 4.6mm x 25 cm, 98:2:0.2 hexane/isopropanol/AcOH, 1.0 mL/min) T_R = 28.9 min (minor), T_R = 36.2 min (major).



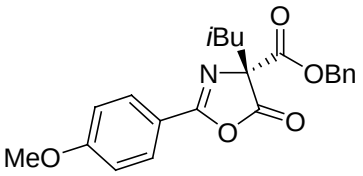
4-Allyl-5-oxo-2-(4-methoxyphenyl)-4,5-dihydrooxazole-4-carboxylic acid phenyl ester (15f). Starting with **13f**, procedure A was followed yielding **15f** as a clear, yellow oil (32 mg, 91%, 91% ee). HPLC (Chiralpak AD, 4.6mm x 25 cm, 90:10:1 hexane/isopropanol/AcOH, 1.0 mL/min) T_R = 21.9 min (minor), T_R = 31.5 min (major). Analytical tlc, 80:20:1 hexane/Et_2O/AcOH, Rf= 0.32. Molecular ion calculated for $C_{20}H_{17}NO_5$: 351.1107; [M^+], EIMS found m/z= 351.1106; IR (neat, cm^{-1}) 1823, C=O; 1645, C=O; 1513, C=N; 400 MHz NMR ($CDCl_3$, ppm) δ 7.99-7.97 (2 H, m) 7.35-7.30 (2 H, m) 7.22-7.18 (1 H, m) 7.07-7.05 (2 H, m) 6.97-6.95 (2 H, m) 5.72-5.62 (1 H, m) 5.29-5.12 (2 H, m) 3.85 (3 H, s) 3.15-2.95 (2 H, m). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 173.9, 164.5, 164.0, 163.5, 150.4, 130.6, 129.7, 129.4, 126.7, 122.1, 121.3, 117.5, 114.6, 55.8, 38.6, 29.9.



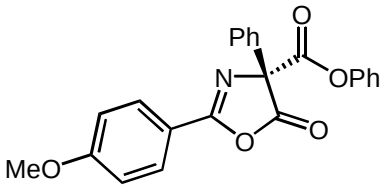
4-Allyl-5-oxo-2-(4-methoxyphenyl)-4,5-dihydrooxazole-4-carboxylic acid benzyl ester (15i). Starting with **13i**, procedure B was followed yielding the known compound **15i** [8] as a clear, yellow oil (33 mg, 91%, 90% ee). HPLC (Regis Whelk-O, 4.6mm x 25 cm, 98:2:0.2 hexane/isopropanol/AcOH, 1.0 mL/min) T_R = 22.8 min (minor), T_R = 26.1 min (major).



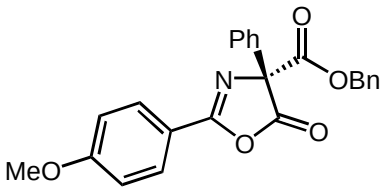
4-Isobutyl-5-oxo-2-(4-methoxyphenyl)-4,5-dihydrooxazole-4-carboxylic acid phenyl ester (15g). Starting with **13g**, procedure A was followed yielding **15g** as a clear, colorless oil (33 mg, 90%, 91% ee). HPLC (Regis Whelk-O, 4.6mm x 25 cm, 95:5:0.1 hexane/isopropanol/AcOH, 1.0 mL/min) T_R = 11.5 min (minor), T_R = 12.7 min (major). Analytical tlc, 80:20:1 hexane/Et_2O/AcOH, Rf= 0.37. Molecular ion calculated for $C_{21}H_{22}NO_5$: 368.1493; [M+H], EIMS found m/z= 368.1504; IR (neat, cm^{-1}) 1822, C=O; 1649, C=O; 1513, C=N; 400 MHz NMR ($CDCl_3$, ppm) δ 8.05-8.03 (2 H, m) 7.38-7.34 (2 H, m) 7.25-7.22 (1 H, m) 7.10-7.08 (2 H, m) 7.02-7.00 (2 H, m) 3.89 (3 H, s) 2.49 (1 H, dd, J= 14.0, 5.5 Hz) 2.16 (1 H, dd, J= 14.0, 7.0 Hz) 1.86-1.76 (1 H, m) 1.00 (3 H, d, J= 6.6 Hz) 0.96 (3 H, d, J= 6.6 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 175.0, 165.0, 163.9, 163.0, 150.5, 130.5, 129.7, 126.6, 121.3, 117.6, 114.6, 76.5, 55.7, 42.9, 24.9, 24.0, 23.3.



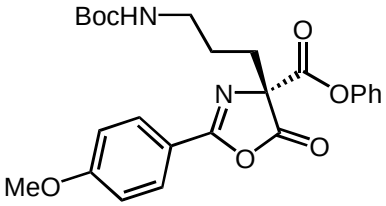
4-Isobutyl-5-oxo-2-(4-methoxyphenyl)-4,5-dihydrooxazole-4-carboxylic acid benzyl ester (15j). Starting with **13j**, procedure B was followed yielding the known compound **15j** [8] as a clear, colorless oil (33 mg, 87%, 92% ee). HPLC (Regis Whelk-O, 4.6mm x 25 cm, 98:2:0.2 hexane/isopropanol/AcOH, 1.0 mL/min) T_R = 18.9 min (minor), T_R = 21.0 min (major).



4-Phenyl-5-oxo-2-(4-methoxyphenyl)-4,5-dihydrooxazole-4-carboxylic acid phenyl ester (15h). Starting with **13h**, procedure A was followed without silica gel isolation yielding **15h** as a yellow solid. Compound **15h** proved unstable to silica, however, NMR showed only a single dominant product with trace impurities, and HPLC showed only the two peaks expected (58% ee) based on comparison to the racemate. HPLC (Chiralpak AD, 4.6mm x 25 cm, 90:10:0.1 hexane/isopropanol/AcOH, 1.0 mL/min) T_R = 14.3 min (minor), T_R = 23.4 min (major). Analytical tlc, 1:1 hexane/Et_2O, Rf= 0.50. Molecular ion calculated for $C_{23}H_{17}NO_5$: 387.1107; [M^+], EIMS found m/z= 387.1115; IR (neat, cm^{-1}) 1819, C=O; 1642, C=O; 1513, C=N; 500 MHz NMR ($CDCl_3$, ppm) δ 8.12 (2 H, d, J= 8.8 Hz) 7.85-7.83 (2 H, m) 7.47-7.40 (3 H, m) 7.36-7.33 (2 H, m) 7.24-7.21 (1 H, m) 7.10-7.08 (2 H, m) 7.03 (2 H, d, J= 8.8 Hz) 3.90 (3 H, s). ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 172.8, 164.7, 164.2, 163.7, 150.7, 133.8, 130.8, 129.7, 129.6, 129.1, 126.8, 126.7, 121.2, 117.8, 114.6, 77.8, 55.8.

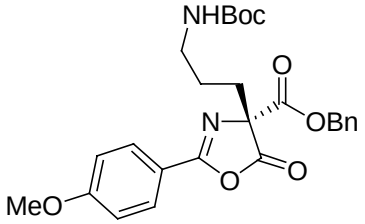


4-Phenyl-5-oxo-2-(4-methoxyphenyl)-4,5-dihydrooxazole-4-carboxylic acid benzyl ester (15k). Starting with **13k**, procedure B was followed except that the 10:1:0.1 hexane/EtOAc/AcOH was used as column eluent yielding the compound **15k** as a clear, yellow oil (38.4 mg, 96%, 20% ee). HPLC (Chiralpak AD, 4.6mm x 25 cm, 90:10:1 hexane/isopropanol/AcOH, 1.0 mL/min) T_R = 12.3 min (minor), T_R = 28.34 min (major). Analytical tlc, 1:1 hexane/Et_2O, Rf= 0.45. Molecular ion calculated for $C_{24}H_{20}NO_5$: 402.1336; [M+H], EIMS found m/z= 402.1348; IR (neat, cm^{-1}) 1817, C=O; 1754, C=O; 1512, C=N; 500 MHz NMR ($CDCl_3$, ppm) δ 8.07-8.04 (2 H, m) 7.75-7.71 (2 H, m) 7.41-7.23 (8 H, m) 7.00-6.97 (2 H, m) 5.25-5.23 (2 H, m) 3.86 (3 H, s). ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 173.0, 165.9, 164.1, 163.4, 135.0, 134.1, 130.7, 129.4, 128.9, 128.8, 128.6, 128.0, 126.8, 117.6, 114.6, 77.8, 68.6, 55.8.

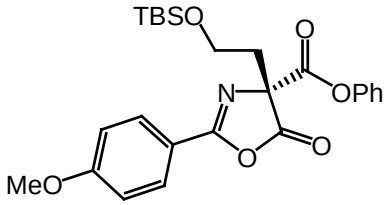


4-(3-*tert*-butoxycarbonylamino-propyl)-5-oxo-2-(4-methoxyphenyl)-4,5-dihydrooxazole-4-carboxylic acid phenyl ester (21b). Starting with **20b**, procedure A was followed yielding **21b** as a clear, colorless oil (43 mg, 92%, 91% ee). HPLC (Chiralpak AD, 4.6mm x 25 cm, 90:10 hexane/isopropanol, 1.0 mL/min) T_R = 21.8 min (minor), T_R = 41.6 min (major). Analytical tlc, 66:33:0.1 hexanes/ether/AcOH, Rf= 0.33. Molecular ion calculated for $C_{25}H_{29}N_2O_7$: 469.19740 [M+H]; EIMS found m/z= 469.1977, error= 1 ppm; IR (neat, cm^{-1}) 1820, C=O; 1769, C=O;

1513, C=N; 500 MHz ^{1}H NMR ($CDCl_3$, ppm) δ 8.05-8.03 (2 H, m) 7.40-7.36 (2 H, m) 7.27-7.25 (1 H, m) 7.12-7.11 (2 H, m) 7.03-7.02 (2 H, m) 4.61 (1 H, br s) 3.91 (3 H, s) 3.26-3.19 (2 H, m) 2.48-2.41 (1 H, m) 2.33-2.27 (1 H, m) 1.71-1.52 (2 H, m) 1.44 (9 H, s). ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 174.4, 164.7, 164.1, 156.1, 150.4, 130.7, 129.8, 126.8, 121.3, 117.4, 114.6, 76.5, 55.8, 28.6.

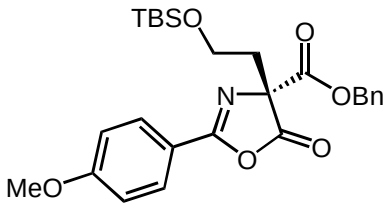


4-(3-*tert*-butoxycarbonylamino-propyl)-5-oxo-2-(4-methoxyphenyl)-4,5-dihydrooxazole-4-carboxylic acid benzyl ester (21a). Starting with **20a**, procedure B was followed except that no purification was performed other than concentration (aspirator) yielding compound **21a** as a clear, yellow oil. This material was carried on to lactam **23a** without purification.

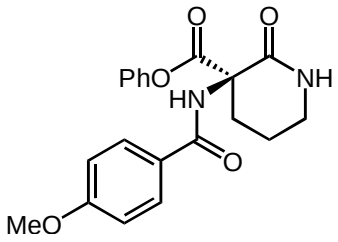


4-[2-(*tert*-butyldimethylsilanyloxy)-ethyl]-5-oxo-2-(4-methoxyphenyl)-4,5-dihydrooxazole-4-carboxylic acid phenyl ester (28b). Starting with **27b** (100 mg, 0.210 mmol), procedure A was followed (using 1 mg of (*R*)-**1**, in 4 mL *t*-amyl alcohol) yielding **28b** as a clear, colorless oil (95 mg, 95%, 91% ee). HPLC (Regis Whelk-O, 4.6mm x 25 cm, 90:10 hexane/isopropanol, 1.0 mL/min) T_R = 7.2 min (minor), T_R = 8.4 min (major). Analytical tlc, 75:23:2 hexanes/ether/AcOH, Rf= 0.30. Molecular ion calculated for $C_{25}H_{31}NO_6Si$: 469.19207 [M^+]; EIMS found m/z=; IR (neat, cm^{-1}) 1827, C=O; 1764, C=O; 1513, C=N; 500 MHz ^{1}H NMR ($CDCl_3$, ppm) δ 8.04 (2 H, d, 8.7 Hz) 7.38-7.35 (2 H, m) 7.25-7.22 (1 H, m) 7.11-7.09 (2 H, m)

7.01 (2 H, d, J= 8.7 Hz) 3.90 (3 H, s) 3.77-3.71 (2 H, m) 2.77-2.65 (2 H, m) 0.82 (9 H, s) –0.02 (3 H, s) –0.13 (3 H, s). ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 174.6, 165.2, 164.0, 163.6, 150.3, 130.3, 129.5, 126.4, 121.1, 117.9, 114.2, 74.1, 58.2, 55.5, 36.6, 25.7, 18.1, -5.9.

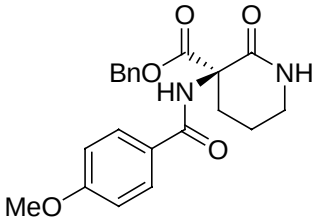


4-[2-(*tert*-butyldimethylsilanyloxy)-ethyl]-5-oxo-2-(4-methoxyphenyl)-4,5-dihydrooxazole-4-carboxylic acid benzyl ester (28a). Starting with **27a**, procedure B was followed yielding the compound **28a** as a clear, yellow oil (49 mg, >95%, 89% ee). HPLC (Chiralpak AD, 4.6mm x 25 cm, 98:2:0.2 hexane/isopropanol/AcOH, 1.0 mL/min) T_R = 17.0 min (minor), T_R = 24.5 min (major). Analytical tlc, 80:20:0.2 hexanes/ether/AcOH, Rf= 0.30. Molecular ion calculated for $C_{26}H_{34}NO_6Si$ [M+H]: 484.21550; found m/z= 484.2158, error= 1 ppm; IR (neat, cm^{-1}) 1824, C=O; 1513, C=N; 1258, C-O; 400 MHz ^{1}H NMR ($CDCl_3$, ppm) δ 7.95-7.92 (2 H, m) 7.32-7.23 (5 H, m) 6.95-6.92 (2 H, m) 5.23-5.11 (2 H, m) 3.84 (3 H, s) 3.65-3.60 (2 H, m) 2.62-2.48 (2 H, s) 0.74 (9 H, s) -0.10 (3 H, s) -0.21 (3 H, s). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 174.8, 166.3, 163.5, 163.4, 134.9, 130.2, 128.5, 128.3, 127.7, 118.0, 114.2, 74.0, 67.9, 58.2, 55.5, 36.6, 25.6, 18.1, -6.0.



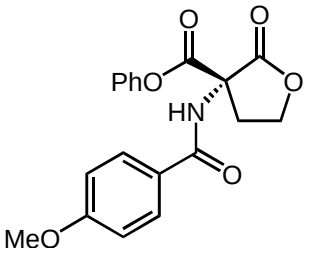
3-(4-Methoxybenzoylamino)-2-oxo-piperidine-3-carboxylic acid phenyl ester (23b). Azlactone **21b** (0.100 mmol estimated, used crude from enol carbonate **20b**) was dissolved in CH_2Cl_2 (1.2 mL), and the solution was cooled to 0 ºC. To this solution was added TFA (0.12 mL, 1.56 mmol, Aldrich), and the solution was stirred at rt for 90 min. The solution was concentrated (N_2; vacuum) and the residue taken up in CH_2Cl_2 (2.4 mL). To this solution was added PBu_3 (0.025 mL, 0.100 mmol, Aldrich) and Et_3N (0.013 mL, 0.100 mmol). The solution was allowed to stir at rt overnight, then quenched with iodomethane (1 mL). The solution was extracted from 0.1 M HCl with CH_2Cl_2. The combined organics were washed with brine, dried over $MgSO_4$, filtered and concentrated (aspirator) yielding a white solid. This residue was purified by preparatory TLC (1mm silica) with 3:1 EtOAc/hexanes as the eluent yielding pure **23b** (0.025 g, 68% over two steps) as a white solid. HPLC (Chiralpak OD, 4.6mm x 25 cm, 75:25 hexanes/EtOH, 1.0 mL/min) T_R = 9.3 min (major), T_R = 17,1 min (minor). Analytical tlc, 6:1 EtOAc/hexanes, Rf= 0.28. Molecular ion calculated for $C_{20}H_{20}N_2O_5Na$: 391.14230 [M+Na]; ESMS found m/z= 391.1; IR (neat, cm^{-1}) 1653, C=O; 1191, C-O; 500 MHz ^1H NMR ($CDCl_3$, ppm) δ 7.84-7.82 (2 H, m) 7.68 (1 H, br s) 7.41-7.36 (2 H, m) 7.28-7.24 (1 H, m) 7.14-7.11 (2 H, m) 6.94-6.92 (2 H, m) 6.50 (1 H, br s) 3.85 (3 H, s) 3.72-3.66 (1 H, m) 3.50-3.45 (1 H, m) 2.72-2.66 (1 H, m) 2.59-2.52 (1 H, m) 2.46-2.37 (1 H, m) 2.03-1.98 (1 H, m). ^{13}C NMR (126 MHz,

$CDCl_3$, ppm) δ 169.4, 167.3, 166.4, 162.8, 150.6, 129.8, 129.3, 126.7, 125.9, 121.4, 114.0, 62.7, 55.6, 42.1, 31.8, 21.0.



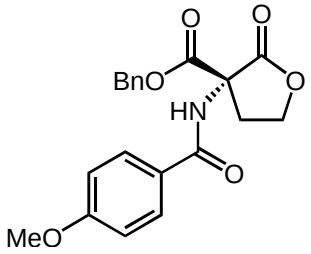
3-(4-Methoxybenzoylamino)-2-oxo-piperidine-3-carboxylic acid benzyl ester (23a). Azlactone **21a** (0.100 mmol estimated, used crude from enol carbonate **20a**) was dissolved in CH_2Cl_2 (1.2 mL), and the solution was cooled to 0 ºC. To this solution was added TFA (0.12 mL, 1.56 mmol, Aldrich), and the solution was stirred at rt for 90 min. The solution was concentrated (N_2 and vacuo) and the residue taken up in CH_2Cl_2 (2.4 mL). To this solution was added DMAP (2.0 mg, 0.016 mmol, Aldrich) and Et_3N (0.027 mL, 0.200 mmol). The solution was allowed to stir at rt overnight, then quenched with iodomethane (1 mL). The solution was extracted from 0.1 M HCl with CH_2Cl_2. The combined organics were washed with brine, dried over $MgSO_4$, filtered and concentrated (aspirator) yielding a white solid. This residue was purified by preparatory TLC (1 mm silica) with 3:1 EtOAc/hexanes as the eluent yielding pure **23a** (0.030 g, 78% over two steps, 92% ee) as a white solid. HPLC (Chiralpak OD, 4.6mm x 25 cm, 75:25 hexane/EtOH, 1.0 mL/min) T_R = 9.2 min (major), T_R = 18.2 min (minor). Analytical tlc, 7:1 EtOAc/hexanes, Rf= 0.3. Molecular ion calculated for $C_{21}H_{22}N_2O_5Na$: 405.1426 [M+Na]; ESMS found m/z= 405.2; IR (neat, cm^{-1}) 1744, C=O; 1733, C=O; 1652, C=O; 400 MHz ^1H NMR ($CDCl_3$, ppm) δ 7.80 (2 H, d, J= 9.2 Hz) 7.63 (1 H, br s) 7.41-7.29 (5 H, m) 6.92 (2 H, d, J= 9.2 Hz) 6.20 (1 H, br s) 5.34 (1 H, d, J= 12.0 Hz) 5.24 (1 H, d, J= 12.0 Hz) 3.85 (3 H, s) 3.71-3.58 (1 H, m) 3.42-3.32 (1 H, m) 2.57-2.44 (1 H, m) 2.37-2.13 (2 H, m) 1.93-1.81 (1 H,

m). ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 170.3, 167.2, 165.9, 162.5, 134.8, 129.1, 128.7, 128.5, 128.0, 125.7, 113.7, 68.3, 62.3, 55.4, 41.9, 31.6, 20.9.



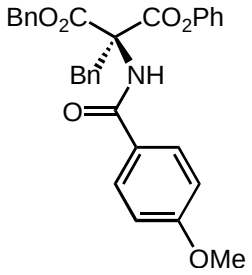
3-(4-Methoxybenzoylamino)-2-oxo-tetrahydro-furan-3-carboxylic acid phenyl ester (30b). Azlactone **28b** (90 mg, 0.191 mmol) was dissolved in THF (5 mL) and this solution was cooled to 0 ºC. To this solution was added HF•pyridine (0.50 mL) and the resulting solution was allowed to warm to rt overnight. The solution was extracted from sat aq $NaHCO_3$ with Et_2O. The combined organics were washed with brine, dried over $MgSO_4$, filtered and concentrated (aspirator). The residue was taken up in toluene and concentrated (aspirator) in order to remove pyridine. The residue was purified by flash chromatography with 1:1 EtOAc/hexanes as the eluent yielding **30b** (57 mg, 85%, >83% ee). HPLC (Chiralpak AD, 4.6mm x 25 cm, 85:15 hexane/EtOH, 1.0 mL/min) T_R = 17.9 min (major), T_R = 23.4 min (minor). Analytical tlc, 1:1 hexane/EtOAc, Rf= 0.31. Molecular ion calculated for $C_{19}H_{17}NO_6Na$: 378.10550 [M+Na]; ESMS found m/z= 378.1; IR (neat, cm^{-1}); 1755, C=O; 1027, C-O; 500 MHz ^{1}H NMR ($CDCl_3$, ppm) δ 7.83-7.81 (2 H, m) 7.44-7.28 (4 H, m) 7.13-7.12 (2 H, m) 6.97-6.94 (2 H, m) 4.80-4.67 (2 H, m) 3.87 (3 H, s) 3.21-3.16 (1 H, m) 2.98-2.91 (1 H, m). ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 171.3, 167.1, 166.8, 163.3, 150.2, 130.0, 129.5, 127.1, 124.8, 121.2, 121.1, 114.2, 77.5, 67.2, 63.5, 55.7, 33.8. Treatment of azlactone **28b** with TBAF led to the formation of lactone **31**, which was identified via preparation of the material independently according to the following procedure. α-Amino-γ-butyrolactone•HBr (4.0 g, 21.98 mmol, Aldrich) was dissolved in

CH_2Cl_2 (55 mL) and Et_3N (7.4 mL) at 0 ºC. To this solution was added a solution of anisoylchloride (3.8 g, 22.27 mmol, Aldrich) as a solution in CH_2Cl_2 (25 mL). The resulting slurry was stirred at 0 ºC for 1 h, then at rt for 4 h. The solution was washed with 0.1 M HCl, sat aq $NaHCO_3$ and brine, dried over $MgSO_4$, filtered an concentrated yielding pure α-amido-γ-butyrolactone **31** (5.077 g, 98%). Analytical tlc, 1:1 EtOAc/hexanes, Rf= 0.11. Molecular ion calculated for $C_{12}H_{13}NO_4Na$: 258.0742 [M+Na]; ESMS found m/z= 258.3; IR (neat, cm^{-1}) 1770, C=O; 1636, C=O; 1176, C-O; 500 MHz ^1H NMR ($CDCl_3$, ppm) δ 7.81 (2 H, d, J= 8.8 Hz) 6.94 (2 H, d, J= 8.8 Hz) 6.72 (1 H, br s) 4.76-4.73 (1 H, m) 4.55-4.53 (1 H, m) 4.39-4.36 (1 H, m) 3.87 (3 H, s) 3.00-2.95 (1 H, m) 2.32-2.28 (1 H, m). ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 178.1, 167.8, 163.1, 129.7, 125.6, 114.1, 66.5, 56.1, 50.4, 31.0.



3-(4-Methoxybenzoylamino)-2-oxo-tetrahydro-furan-3-carboxylic acid benzyl ester (30a). Azlactone **28a** (0.040 g, 0.083 mmol) was dissolved in THF (2 mL) and this solution was cooled to 0 ºC. To this solution was added HF•pyridine (0.20 mL) and the resulting solution was allowed to warm to rt overnight. The solution was extracted from sat aq $NaHCO_3$ with Et_2O. The combined organics were washed with brine, dried over $MgSO_4$, filtered and concentrated (aspirator). The residue was taken up in toluene and concentrated (aspirator) in order to remove pyridine. The residue was purified by preparative TLC (1mm silica) with 1:1 EtOAc/hexanes as the eluent yielding **30a** (0.030 g, 95%, 89% ee). HPLC (Regis Whelk-O, 4.6mm x 25 cm, 90:10 hexane/isopropanol, 1.0 mL/min) T_R = 11.2 min (minor), T_R = 13.7 min (major). Analytical tlc,

1:1 hexane/EtOAc, Rf= 0.30. Molecular ion caclulated for $C_{20}H_{19}NO_6Na$: 392.12120 [M+Na]; ESMS found m/z= 392.2;; IR (neat, cm^{-1}) 1779, C=O; 1606, C=O; 1257, C-O; 400 MHz ^1H NMR ($CDCl_3$, ppm) δ 7.80-7.77 (2 H, m) 7.39-7.32 (5 H, m) 6.95-6.92 (2 H, m) 5.37-5.24 (2 H, m) 4.71-4.65 (1 H, m) 4.54-4.48 (2 H, m) 3.85 (3 H, s) 2.93-2.77 (2 H, m). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 171.1, 167.9, 166.1, 162.9, 134.1, 129.2, 128.9, 128.8, 128.1, 124.7, 113.9, 93.1, 69.0, 66.6, 63.0, 55.4, 32.9.

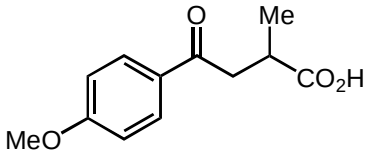


2-(4-Methoxybenzoylamino)-2-methyl-malonic acid benzyl ester phenyl ester . A solution of **15b** (0.100 mmol, 88% ee, prepared using (*S*)-**1**) in CH_2Cl_2 (1 mL) at 0 °C was treated with benzoic acid (2.4 mg, 0.02 mmol), benzyl alcohol (0.013 mL, 0.12 mmol), and PBu_3 (0.025 mL, 0.100 mmol). The solution was allowed to warm to rt and stir overnight, and was then quenched with iodomethane (0.1 mL) and extracted from sat aq $NaHCO_3$ with CH_2Cl_2. The combined organic layers were washed with brine, dried over $MgSO_4$ filtered and concentrated (aspirator). The residue was purified via preparative TLC (silica gel, 1mm x 20cm x 20cm; 1:1 EtOAc/hexane) to yield the malonate diester as a clear, colorless oil (38 mg, 85%, 88% ee). HPLC (Chiracel OJ, 4.6mm x 25 cm, 80:20 hexane/isopropanol, 1.0 mL/min) T_R = 15.3 min (major), T_R = 39.1 min (minor). Analytical tlc, 1:2 EtOAc/hexane, Rf= 0.30. Molecular ion calculated for $C_{25}H_{23}NNaO_6$: 456.1423; [M+Na], ESMS found m/z= 456.2; IR (neat, cm^{-1}) 1741, C=O; 1656, C=O; 1606, C=O; 500 MHz NMR ($CDCl_3$, ppm) δ 7.85-7.80 (2 H, m) 7.53 (1 H, br s) 7.40-7.34 (5 H, m) 7.31-7.27 (2 H, m) 7.21-7.19 (1 H, m) 6.95-6.92 (2 H, m) 6.88-6.86 (2 H,

m) 5.39 (1 H, d, J= 12.2 Hz) 5.30 (1 H, d, J= 12.2 Hz) 3.84 (3 H, s) 2.00 (3 H, s). ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 169.2, 167.4, 165.9, 162.9, 150.8, 135.0, 129.6, 129.3, 129.0, 128.7, 126.4, 125.7, 121.5, 114.1, 68.7, 63.6, 55.7, 21.5.

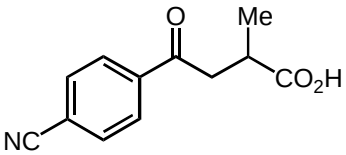
Correlation of absolute configuration of 15b and *ent*-15a. The same major enantiomer was also prepared by an independent route. Thus, *ent*-**15a** (34 mg, 0.100 mmol, 86% ee) as a solution in CH_2Cl_2 (1 mL) was treated with benzoic acid (2.4 mg, 0.020 mmol), phenol (12mg, 0.128 mmol) and PBu_3 (0.025 mL, 0.100 mmol) at 0 °C. The solution was allowed to warm to rt and stir overnight. The reaction was quenched with iodomethane (0.1 mL) and extracted from sat aq $NaHCO_3$ with CH_2Cl_2. The combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated (aspirator). The residue was purified via preparative TLC (silica gel, 1mm x 20cm x 20cm; 1:1 EtOAc/hexane) to yield malonate diester as a clear, colorless oil (30 mg, 70%, 86% ee). Using the same assay method as above, the same order of retention times was seen for major and minor enantiomers.

Preparation of Furanone Enol Carbonates



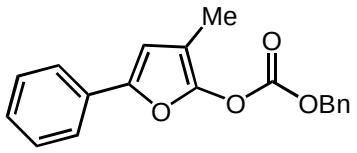
4-(4-Methoxyphenyl)-2-methyl-4-oxo-butyric acid. To a solution of *i*Pr_2NH (1.4 mL, 9.99 mmol, Aldrich) in THF (20 mL) was added *n*BuLi (6.4 mL, 1.55 M in hexane, 9.92 mmol, Acros) at 0 °C. After 15 min the solution was cooled to –78 °C and treated with 4-methoxyacetophenone (1.34 g, 8.96 mmol) as a solution in THF (15 mL). The solution was allowed to stir at –78 °C for 30 min, then treated with a solution of freshly prepared ethyl lactate triflate[13] (2.69 g, 10.8 mmol) in THF (15 mL). The solution was allowed to warm to rt, then

poured into 0.1 M HCl and extracted with Et_2O. The combined organic layers were washed with sat aq $NaHCO_3$ and brine, dried over $MgSO_4$, filtered and concentrated (aspirator). The residue was purified by flash chromatography (silica gel) with 10:90 Et_2O/hexane as the eluent yielding ethyl 4-(4-methoxyphenyl)-2-methyl-4-oxo-butyrate as a clear colorless oil (1.09 g) contaminated with traces of 4-methoxyacetophenone. The oil was dissolved in EtOH (12 mL), and to this solution was added a solution of NaOH (1.0 g, 25.0 mmol, Fisher) in H_2O (12 mL) to saponify the ester. After 30 min, the solution was concentrated to approximately half of the original volume (aspirator) and washed with Et_2O to remove neutral organics. The aqueous layer was acidified with conc HCl (12 M, Fisher) to pH < 2 causing a white solid to precipitate. The mixture was extracted with CH_2Cl_2, with the combined organic layers dried over $MgSO_4$, filtered and concentrated (aspirator) yielding 4-(4-methoxyphenyl)-2-methyl-4-oxo-butyric acid as a white crystalline solid (0.877 g, 3.95 mmol, 44% over two steps). Analytical tlc, 3:1 Et_2O/hexane, Rf= 0.14. Molecular ion calculated for $C_{12}H_{14}NaO_4$: 245.0790; [M+Na], ESMS found m/z= 245.1; IR (neat, cm^{-1}) 1673, C=O; 1601, C=O; 1255, C-O; 500 MHz NMR ($CDCl_3$, ppm) δ 11.98 (1 H, br s) 7.97-7.94 (2 H, m) 6.95-6.92 (2 H, m) 3.87 (3 H, s) 3.42 (1 H, dd, J= 17.6, 7.8 Hz) 3.18-3.12 (1 H, m) 3.01 (1 H, dd, J= 17.6, 5.4 Hz) 1.31 (3 H, d, J= 6.8 Hz). ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 196.6, 182.4, 163.9, 130.6, 129.8, 114.0, 55.7, 41.6, 35.1, 17.3.



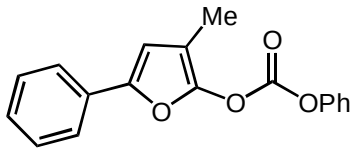
4-(4-Cyanophenyl)-2-methyl-4-oxo-butyric acid. To a solution of LHMDS (1.582, 9.46 mmol, Aldrich) in THF (20 mL) at –78 °C was added 4-cyanoacetophenone (1.34 g, 8.96 mmol, Aldrich) as a solution in THF (15 mL). The solution was allowed to stir at –78 °C for 30 min, then treated with a solution of freshly prepared ethyl lactate triflate[13] (2.69 g, 10.8 mmol) in THF

(15 mL). The solution was allowed to warm to rt, then poured into 0.1 M HCl and extracted with Et_2O. The combined organic layers were washed with sat aq $NaHCO_3$ and brine, dried over $MgSO_4$, filtered and concentrated (aspirator). The residue was purified by flash chromatography (silica gel) with 50:50 Et_2O/hexane as the eluent yielding ethyl 4-(4-cyanophenyl)-2-methyl-4-oxo-butyrate as a clear colorless oil contaminated with ~1 eq of 4-cyanoacetophenone. The oil was dissolved in EtOH (12 mL), and to this solution was added a solution of NaOH (1.0 g, 25.0 mmol, Fisher) in H_2O (12 mL) to saponify the ester. After 30 min, the solution was concentrated to approximately half of the original volume (aspirator) and washed with Et_2O to remove neutral organics. The aqueous layer was acidified with conc HCl (12 M, Fisher) to pH < 2 causing a white solid to precipitate. The mixture was extracted with CH_2Cl_2, with the combined organic layers dried over $MgSO_4$, filtered and concentrated (aspirator) yielding 4-(4-cyanophenyl)-2-methyl-4-oxo-butyric acid as a white crystalline solid (0.467 g, 2.15 mmol, 24% over two steps). Analytical tlc, 95:5 CH_2Cl_2/AcOH, Rf= 0.30. Molecular ion calculated for $C_{12}H_{11}NO_3$: 217.07390 [M+]; EIMS found m/z= 217.0741, error= 1 ppm; IR (neat, cm^{-1}) 1711, C=O; 1690, C=O; 1246, C-O; 500 MHz ^{1}H NMR ($CDCl_3$, ppm) δ 11.7 (1 H, br s) 8.07-8.04 (2 H, m) 7.80-7.72 (2 H, m) 3.51-3.46 (1 H, m) 3.21-3.14 (1 H, m) 3.05-3.00 (1 H, m) 1.34 (3 H, d, J= 6.6 Hz). ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 196.8, 181.8, 139.6, 132.8, 128.7, 118.1, 116.8, 42.1, 34.9, 17.3.



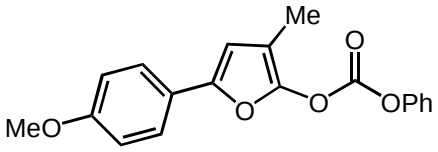
Carbonic acid 5-phenyl-3-methylfuran-2-yl ester benzyl ester (44a). Furanone **43** (Ar = Ph) was prepared according to literature precedent.[14] To a solution of LHMDS (0.423 g, 2.53 mmol, Aldrich) in THF (3 mL) at –78 °C was added a solution of furanone **43** (0.400 g, 2.30 mmol) in

THF (3 mL). This solution was allowed to stir at –78 °C for 30 min, then transferred via cannula to a solution of benzyl chloroformate (0.36 mL, 2.52 mmol, Aldrich) in THF (3 mL). This solution was allowed to warm to rt, then extracted from 0.1 M HCl with Et_2O. The combined organics were washed with brine, dried over $MgSO_4$, filtered and concentrated (aspirator). The residue was purified via flash chromatography (silica, 3 x 15 cm) using 90:10 hexanes/Et_2O as the eluent yielding furanone enol carbonate **44a** (0.574 g, 81%) as clear, colorless crystals. Analytical tlc, 9:1 hexane/ether, Rf= 0.35. Molecular ion calculated for $C_{19}H_{17}O_4$: 309.11260 [M+H]; CIMS found m/z= 309.1134, error= 2 ppm; IR (neat, cm^{-1}) 1777, C=O; 1202, C-O; 500 MHz ^{1}H NMR ($CDCl_3$, ppm) δ 7.61-7.60 (2 H, m) 7.50-7.36 (7 H, m) 7.28-7.25 (2 H, m) 6.54 (1 H, s) 5.35 (2 H, s) 1.98 (3 H, s). ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 152.5, 147.0, 146.8, 134.5, 130.5, 129.3, 129.0, 129.0, 128.9, 127.5, 123.5, 108.9, 104.8, 71.5, 8.7.



Carbonic acid 5-phenyl-3-methylfuran-2-yl ester phenyl ester (44b). Furanone **43** (Ar = Ph) was prepared according to literature precedent.[14] To a solution of LHMDS (0.423 g, 2.53 mmol, Aldrich) in THF (3 mL) at –78 °C was added a solution of furanone **43** (0.400 g, 2.30 mmol) in THF (3 mL). This solution was allowed to stir at –78 °C for 30 min, then transferred via cannula to a solution of phenyl chloroformate (0.32 mL, 2.52 mmol, Aldrich) in THF (3 mL). This solution was allowed to warm to rt, then extracted from 0.1 M HCl with Et_2O. The combined organics were washed with brine, dried over $MgSO_4$, filtered and concentrated (aspirator). The residue was purified via flash chromatography (silica, 3 x 15 cm) using 85:15 hexanes/Et_2O as the eluent yielding furanone enol carbonate **44b** (0.531 g, 78%) as white crystalline solid. Analytical tlc, 85:15 hexane/ether, Rf= 0.35. Molecular ion calculated for $C_{18}H_{14}O_4$: 294.08910

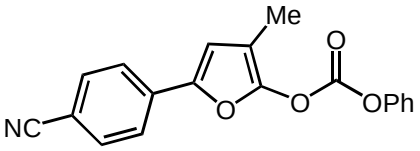
[M+]; EIMS found m/z= 294.0898, error= 2 ppm; IR (neat, cm^{-1}) 1794, C=O; 1187, C-O; 500 MHz ^{1}H NMR ($CDCl_3$, ppm) δ 7.59-7.56 (2 H, m) 7.43-7.21 (8 H, m) 6.50 (1 H, s) 2.00 (3 H, s). ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 151.1, 150.7, 147.2, 146.5, 130.4, 129.9, 129.7, 128.8, 127.5, 126.8, 123.6, 120.8, 108.9, 108.8, 104.9, 8.7.



Carbonic acid 5-(4-methoxyphenyl)-3-methylfuran-2-yl ester phenyl ester (44c). 4-(4-Methoxyphenyl)-2-methyl-4-oxo-butyric acid (0.877 g, 3.95 mmol), acetic anhydride (1.0 mL, 10.6 mmol), and acetic acid (1.3 mL, 22.7 mmol) were mixed and the slurry was heated to 100 °C. After 3 h, the mixture became homogeneous and was concentrated (aspirator). The residue was taken up in toluene and concentrated to remove acetic acid/anhydride residue, yielding 5-(4-methoxyphenyl)-3-methylfuran-2-one (mixture of 3*H*- and 5*H*- isomers) as a white crystalline solid (0.806 g, quantitative). The material was sufficiently pure for the next step and was carried on without additional purification.

To a solution of *i*Pr_2NH (0.27 mL, 1.93 mmol, Aldrich) in THF (2 mL) was added *n*BuLi (1.2 mL, 1.55 M in hexane, 1.86 mmol, Acros) at 0 °C. After 15 min the solution was cooled to –78 °C treated with furanone 5-(4-methoxyphenyl)-3-methylfuran-2-one (0.300 g, 1.469 mmol) as a solution in THF (3 mL). After 30 min at –78 °C, the solution was added dropwise to a solution of phenyl chloroformate (0.24 mL, 1.91 mmol, Aldrich) in THF (3 mL) at –78 °C. The solution was allowed to warm to rt, then poured into 0.1 mL HCl, and extracted with Et_2O. The combined organics were washed with brine, dried over $MgSO_4$ filtered and concentrated (aspirator). The residue was purified by flash chromatography (silica gel) with 12:88 Et_2O/hexane as the eluent, yielding furanone enol carbonate **44c** as a white crystalline solid (0.286 g, 60% yield). Analytical

tlc, 9:1 hexane/Et_2O, Rf= 0.20. Molecular ion calculated for $C_{19}H_{16}O_5$: 324.0998; [M^+], EIMS found m/z= 324.1003; IR (neat, cm^{-1}) 1795, C=O; 1225, C-O; 500 MHz NMR ($CDCl_3$, ppm) δ 7.57-7.55 (2 H, m) 7.48-7.45 (2 H, m) 7.35-7.31 (3 H, m) 6.95-6.93 (2 H, m) 6.41 (1 H, s) 3.84 (3 H, s) 2.04 (3 H, s). ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 159.3, 151.1, 151.0, 147.3, 146.0, 129.9, 126.9, 125.1, 123.5, 120.9, 114.4, 107.3, 104.8, 55.5, 8.8.

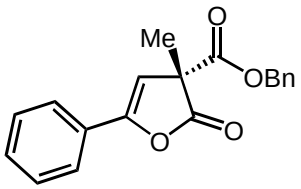


Carbonic acid 5-(4-cyanophenyl)-3-methylfuran-2-yl ester phenyl ester (44d). 4-(4-Cyanophenyl)-2-methyl-4-oxo-butyric acid (0.343 g, 1.58 mmol), acetic anhydride (1.0 mL, 10.6 mmol), and acetic acid (1.3 mL, 22.7 mmol) were mixed and the slurry was heated to 100 °C. After 3 h, the mixture became homogeneous and was concentrated (aspirator). The residue was taken up in toluene and concentrated to remove acetic acid/anhydride residue, yielding 5-(4-cyanophenyl)-3-methylfuran-2-one (mixture of 3*H*- and 5*H*- isomers) as a white crystalline solid (0.315 g, quantitative). The material was sufficiently pure for the next step and was carried on without additional purification.

To a solution of *i*Pr_2NH (0.27 mL, 1.92 mmol, Aldrich) in THF (2.5 mL) was added nBuLi (1.2 mL, 1.60 M in hexane, 1.91 mmol, Acros) at 0 °C. After 15 min the solution was cooled to –78 °C treated with 5-(4-cyanophenyl)-3-methylfuran-2-one (0.315 g, 1.58 mmol) as a solution in THF (2.5 mL). After 30 min at –78 °C, the solution was added dropwise to a solution of phenyl chloroformate (0.24 mL, 1.91 mmol, Aldrich) in THF (2.5 mL) at –78 °C. The solution was allowed to warm to rt, then poured into 0.1 mL HCl, and extracted with Et_2O. The combined organics were washed with brine, dried over $MgSO_4$ filtered and concentrated (aspirator). The residue was purified by flash chromatography (silica gel) with 25:75 Et_2O/hexane as the eluent,

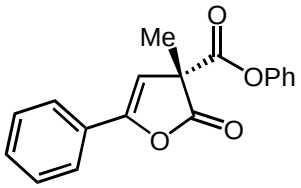
yielding furanone enol carbonate **44d** as a white crystalline solid (0.148 g, 30% yield). Analytical tlc on K6F silica gel 60A, 65:35 hexane/ether, Rf= 0.30. Molecular ion calculated for $C_{19}H_{13}NO_4$: 319.08440 [M+]; EIMS found m/z= 319.0852, error= 2 ppm; IR (neat, cm^{-1}) 1796, C=O; 1216, C-O; 400 MHz ^{1}H NMR ($CDCl_3$, ppm) δ 7.66-7.61 (4 H, m) 7.46-7.29 (5 H, m) 6.68 (1 H, s) 2.04 (3 H, s). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 151.0, 150.5, 147.7, 145.2, 134.2, 132.8, 129.9, 127.0, 123.6, 120.8, 119.1, 112.1, 110.4, 106.0, 8.7.

General Procedure for Furanone Enol Carbonate Rearrangement: A solution of furanone enol carbonate **44** (0.1 M) was treated with TADMAP **1** (10 mol%) and allowed to stir at rt until analytical TLC showed complete consumption of the starting material. The solution was then quenched with iodomethane, and concentrated (aspirator) and the residue separated by flash chromatography and the major regioisomer assayed by HPLC on chiral support.



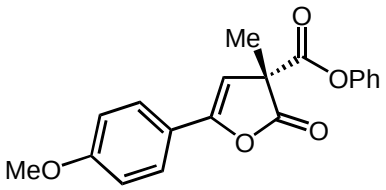
Carboxyl migration of enol carbonate 44a: Enol carbonate **44a** (31 mg, 0.100 mmol) and (*S*)-**1** (4 mg, 0.010 mmol) were dissolved in CH_2Cl_2 (1.0 mL) and allowed to stir for 24 h. The reaction was quenched with iodomethane (0.1 mL). NMR analysis of the crude indicated a ~60:40 mixture of α- and γ-migration products **45a** and **46a**. The solution was then concentrated (N_2 stream) and the residue purified by flash chromatography (silica gel, 1.5 x 15 cm) with 3:1 hexane/Et_2O as the eluent and two products eluted. Fractions containing the first compound to elute were concentrated (aspirator), yielding α-*C*-carboxyl furanone **45a** as a white crystalline solid (20 mg, 64%, 75% ee). HPLC (Chiralpak OJ, 4.6mm x 25 cm, 90:10 hexane/isopropanol, 1.0 mL/min) T_R = 37.6 min (major), T_R = 48.2 min (minor). Analytical tlc, 75:25 hexane/Et_2O,

Rf= 0.25. Molecular ion calculated for $C_{19}H_{16}O_4$: 308.104859; [M^+], EIMS found m/z= 308.1054; IR (neat, cm^{-1}) 1808, C=O; 1742, C=O; 1013, C-O; 500 MHz NMR ($CDCl_3$, ppm) δ 7.59-7.56 (2 H, m) 7.39-7.22 (8 H, m) 5.82 (1 H, s) 5.16 (2 H, d, J= 4.2 Hz) 1.66 (3 H, s). ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 174.7, 168.2, 154.2, 135.0, 130.3, 128.8, 128.6, 128.4, 127.8, 127.6, 125.1, 104.1, 67.8, 55.8, 20.4. Fractions containing the second compound to elute were concentrated (aspirator), yielding γ-*C*-carboxyl furanone **46a** as a clear, colorless oil. Analytical tlc, 1:1 hexane/Et_2O, Rf= 0.25. Molecular ion calculated for $C_{19}H_{17}O_4$: 309.11268; [M+H], CIMS found m/z= 309.1127; IR (neat, cm^{-1}) 1771, C=O; 1221, C-O; 400 MHz NMR ($CDCl_3$, ppm) δ 7.43-7.40 (3 H, m) 7.34-7.26 (5 H, m) 7.22-7.18 (2 H, m) 5.15 (2 H, s) 1.92 (3 H, s). ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 172.1, 167.3, 146.9, 135.4, 134.7, 130.3, 129.3, 128.9, 128.6, 128.5, 128.0, 125.8, 87.6, 68.1, 10.7.



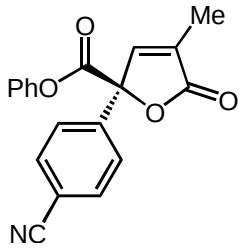
Carboxyl migration of enol carbonate 44b: Enol carbonate **44b** (31 mg, 0.100 mmol) and (*S*)-**1** (4 mg, 0.010 mmol) were dissolved in CH_2Cl_2 (1.0 mL) and allowed to stir for 24 h. The reaction was quenched with iodomethane (0.1 mL). NMR analysis of the crude indicated a ~60:40 mixture of α- and γ–migration products **45b** and **46b**. The solution was then concentrated (N_2 stream) and the residue purified by flash chromatography (silica gel, 1.5 x 15 cm) with 3:1 hexane/Et_2O as the eluent and two products eluted. Fractions containing the first compound to elute were concentrated (aspirator), yielding α-*C*-carboxyl furanone **45b** as a white crystalline solid (9.7 mg, 33%, 91% ee). HPLC (Regis Whelk-O, 4.6mm x 25 cm, 90:10 hexane/isopropanol, 1.0 mL/min) T_R = 11.5min (minor), T_R = 12.8 min (major). Analytical tlc,

80:20 hexane/Et_2O, Rf= 0.25. Molecular ion calculated for $C_{18}H_{14}O_4$: 294.089209; [M^+], EIMS found m/z= 294.0892; IR (neat, cm^{-1}) 1806, C=O; 1758, C=O; 1187, C-O; 500 MHz NMR ($CDCl_3$, ppm) δ 7.71-7.69 (2 H, m) 7.48-7.46 (3 H, m) 7.40-7.37 (2 H, m) 7.27-7.24 (1 H, m) 7.12-7.11 (2 H, m) 6.03 (1 H, s) 1.82 (3 H, s). ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 174.5, 167.0, 154.7, 150.4, 130.4, 129.5, 128.9, 127.5, 126.4, 125.2, 121.1, 103.8, 55.9, 20.4. Fractions containing the second compound to elute were concentrated (aspirator), yielding γ-*C*-carboxyl furanone **46b** as a clear, colorless oil. Analytical tlc, 80:20 hexane/Et_2O, Rf= 0.10. Molecular ion calculated for $C_{18}H_{14}O_4$: 294.089209; [M^+], EIMS found m/z= 294.0903; IR (neat, cm^{-1}) 1771, C=O; 1189, C-O; 400 MHz NMR ($CDCl_3$, ppm) δ 7.58-7.55 (3 H, m) 7.44-7.39 (3 H, m) 7.34-7.30 (2 H, m) 7.20-7.18 (1 H, m) 7.00-6.98 (2 H, m) 1.99 (3 H, s). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 171.9, 166.0, 150.1, 146.5, 135.2, 130.8, 129.8, 129.5, 129.0, 128.7, 128.5, 126.5, 125.7, 120.8, 87.4, 10.6.



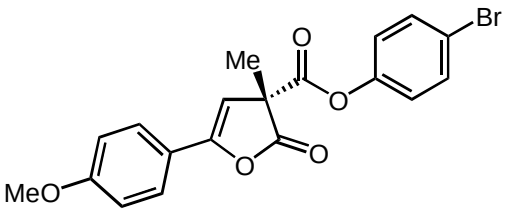
Carboxyl migration of enol carbonate 44c: Enol carbonate **44c** (53 mg, 0.163 mmol) and (*S*)-**1** (7.3 mg, 0.017 mmol) were dissolved in THF (1.6 mL) and allowed to stir for 24 h. The reaction was quenched with iodomethane (0.1 mL). The solution was then concentrated (N_2 stream) and the residue purified by flash chromatography (silica gel) with 3:1 hexane/Et_2O as the eluent and two products eluted. Fractions containing the first compound to elute were concentrated (aspirator), yielding α-*C*-carboxyl furanone **45c** as a white crystalline solid (44 mg, 83%, 90% ee). HPLC (Chiralpak AD, 4.6mm x 25 cm, 90:10 hexane/isopropanol, 1.0 mL/min) T_R = 11.0 min (major), T_R = 17.4 min (minor). Analytical tlc, 70:30 hexane/Et_2O, Rf= 0.35. Molecular ion

calculated for $C_{19}H_{16}O_5$: 324.0998; [M^+], EIMS found m/z= 324.1000; IR (neat, cm^{-1}) 1804, C=O; 1768, C=O; 1186, C-O; 500 MHz NMR ($CDCl_3$, ppm) δ 7.62 (2 H, d, J= 8.8 Hz) 7.40-7.37 (2 H, m) 7.28-7.24 (1 H, m) 7.10 (2 H, d, J= 7.8 Hz) 6.97 (2 H, d, J= 8.8 Hz) 5.85 (1 H, s) 3.87 (3 H, s) 1.80 (3 H, s). ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 174.9, 167.5, 161.4, 154.7, 150.6, 129.7, 127.0, 126.5, 121.3, 120.3, 114.4, 101.7, 56.1, 55.6, 20.6. Fractions containing the second compound to elute were concentrated (aspirator), yielding γ-*C*-carboxyl furanone **46c** as a white crystalline solid. (4 mg, 7%, 80% ee). HPLC (Chiralpak AD, 4.6mm x 25 cm, 90:10 hexane/isopropanol, 1.0 mL/min) T_R = 18.8 min (minor), T_R = 22.9 min (major). Analytical tlc, 1:1 hexane/Et_2O, Rf= 0.33. Molecular ion calculated for $C_{19}H_{16}O_5$: 324.0998; [M^+], EIMS found m/z= 324.0992; IR (neat, cm^{-1}) 1770, C=O; 1178, C-O; 500 MHz NMR ($CDCl_3$, ppm) δ 7.57 (1 H, q, J= 1.5 Hz) 7.52-7.50 (2 H, m) 7.37-7.34 (2 H, m) 7.26-7.22 (1 H, m) 7.04-7.02 (2 H, m) 6.97-6.95 (2 H, m) 3.83 (3 H, s) 2.03 (3 H, d, J= 1.5 Hz). ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 172.3, 166.5, 160.6, 150.4, 146.8, 131.0, 129.8, 127.6, 127.5, 126.7, 121.2, 114.6, 87.5, 55.6, 11.0.



Carboxyl migration of enol carbonate 44d: Enol carbonate **44d** (46 mg, 0.144 mmol) and (*R*)-**1** (6.0 mg, 0.014 mmol) were dissolved in Et_2O (1.4 mL) and allowed to stir for 24 h. The reaction was quenched with iodomethane (0.1 mL). The solution was then concentrated (N_2 stream) and the residue purified by flash chromatography (silica gel) with 1:1 hexane/Et_2O as the eluent and two products eluted. Fractions containing the first compound to elute were concentrated (aspirator), yielding α-*C*-carboxyl furanone **45d** as a white crystalline solid (11 mg,

24%). Analytical tlc, 1:1 hexane/ether, Rf= 0.20. Molecular ion calculated for $C_{19}H_{13}NO_4$: 319.08440 [M+]; EIMS found m/z= 319.0837, error= 2 ppm; IR (neat, cm^{-1}) 1810, C=O; 1759, C=O; 1187, C-O; 500 MHz ^{1}H NMR ($CDCl_3$, ppm) δ 7.80-7.74 (4 H, m) 7.40-7.37 (2 H, m) 7.28-7.25 (1 H, m) 7.10-7.08 (2 H, m) 6.18 (1 H, s) 1.82 (3 H, s). ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 173.7, 166.6, 153.1, 150.5, 132.9, 131.7, 129.8, 126.8, 126.0, 121.3, 118.3, 114.1, 107.4, 56.3, 20.6. Fractions containing the second compound to elute were concentrated (aspirator), yielding γ-*C*-carboxyl furanone **46d** as a white crystalline solid. (35 mg, 76%, 90% ee). HPLC (Chiralpak AS, 4.6mm x 25 cm, 95:5 hexane/EtOH, 1.0 mL/min) T_R = 38.1 min (minor), T_R = 45.9 min (major). Analytical tlc, 1:1 hexane/ether, Rf= 0.14. Molecular ion calculated for $C_{19}H_{13}NO_4$: 319.08440 [M+]; EIMS found m/z= 319.0847, error= 1 ppm; IR (neat, cm^{-1}) 1774, C=O; 1189, C-O; 500 MHz ^{1}H NMR ($CDCl_3$, ppm) δ 7.78-7.75 (4 H, m) 7.55-7.54 (1 H, m) 7.39-7.35 (2 H, m) 7.29-7.25 (1 H, m) 7.04-7.00 (2 H, m) 2.00 (3 H, s). ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 171.6, 165.5, 150.2, 145.8, 140.2, 133.0, 131.9, 129.9, 127.0, 121.0, 118.2, 113.8, 86.9, 11.0.

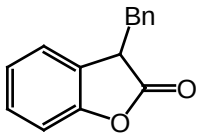


Preparation of 5-(4-Methoxyphenyl)-3-methyl-2-oxo-2,3-dihydrofuran-3-carboxylic acid 4-bromophenyl ester (45e): Furanone **45e** was prepared similar to compound **45c** using (*R*)-**1**. Furanone **45e** (30 mg) was dissolved in a minimal amount of Et_2O (~0.3 mL) and placed in a chamber full of hexanes. After 2 days, crystals had formed and these were subjected to X-ray analysis. Stereochemistry was determined to be (*R*)- **45e** by anomalous dispersion. The stereochemistry of furanones **45a-d** were assigned by analogy. Analytical tlc, 1:1 hexane/ether,

Rf= 0.35. Molecular ion calculated for $C_{19}H_{15}BrO_5$: 402.0102 [M+]; EIMS found m/z= 402.0087, error= 3 ppm; IR (neat, cm^{-1}) 1804, C=O; 1760, C=O; 500 MHz ^1H NMR ($CDCl_3$, ppm) δ 7.63-7.60 (2 H, m) 7.50-7.48 (2 H, m) 7.07-6.96 (4 H, m) 5.83 (1 H, s) 3.90 (3 H, s) 1.80 (3 H, s). ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 174.8, 167.2, 161.6, 154.9, 149.6, 132.7, 127.1, 123.2, 120.2, 119.8, 114.5, 101.5, 56.1, 55.7, 20.7.

3-Alkyl Benzofuranone Enol Carbonate Synthesis & Carboxyl Migration

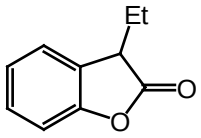
3-Methylbenzofuranone (**38**, R^1 = Me) was prepared according to literature precedent.[15] Known benzofuranones (**38**, R^1 = alkyl)[16] were synthesized using a procedure adapted from Tegeler and coworkers[17] as detailed below.



3-Benzylbenzofuranone. To a slurry of NaH (0.62 g, 15.5 mmol, Aldrich) in DMF (3 mL) was added (2-methoxyphenyl)acetonitrile (2 g, 13.6 mmol, Aldrich). After 1 h at rt, the solution was cooled treated with benzyl bromide (1.6 mL, 13.5 mmol, Aldrich). The solution was allowed to stir overnight, then neutralized with sat aq NH_4Cl and extracted with Et_2O. The combined organics were washed with water and brine, dried over $MgSO_4$, filtered and concentrated (aspirator). The α-branched acetonitrile was sufficiently pure for the next step and was carried on without purification.

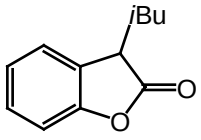
The neat α-branched acetonitrile was poured into a 48 wt% solution of HBr in water and heated to reflux for 48 h. The solution was then cooled to rt and neutralized with NaOH. The solution was extracted with Et_2O. The combined organic layers were washed with brine, dried

over $MgSO_4$, filtered and concentrated (aspirator) and the residue purified by flash chromatography (silica, 5 x 15 cm) with 10:1 hexanes/Et_2O as the eluent yielding known 3-benzylbenzofuranone (1.278 g, 42%).[16]



3-Ethylbenzofuranone. To a slurry of NaH (0.62 g, 15.5 mmol, Aldrich) in DMF (3 mL) was added (2-methoxyphenyl)acetonitrile (2 g, 13.6 mmol, Aldrich). After 1 h at rt, the solution was cooled treated with ethyl iodide (1.1 mL, 13.8 mmol, Aldrich). The solution was allowed to stir overnight, then neutralized with sat aq NH_4Cl and extracted with Et_2O. The combined organics were washed with water and brine, dried over $MgSO_4$, filtered and concentrated (aspirator). The α-branched acetonitrile was sufficiently pure for the next step and was carried on without purification.

The neat α-branched acetonitrile was poured into a 48 wt% solution of HBr in water and heated to reflux for 48 h. The solution was then cooled to rt and neutralized with NaOH. The solution was extracted with Et_2O. The combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated (aspirator) and the residue purified by flash chromatography (silica, 5 x 15 cm) with 10:1 hexanes/Et_2O as the eluent yielding known 3-ethylbenzofuranone (1.268 g, 58%).[16]



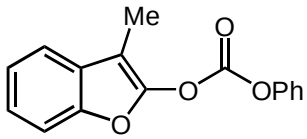
3-Isobutylbenzofuranone. To a slurry of NaH (0.62 g, 15.5 mmol, Aldrich) in DMF (3 mL) was added (2-methoxyphenyl)acetonitrile (2 g, 13.6 mmol, Aldrich). After 1 h at rt, the solution was cooled treated with isobutyl iodide (1.6 mL, 13.9 mmol, Aldrich). The solution was allowed to

stir overnight, then neutralized with sat aq NH_4Cl and extracted with Et_2O. The combined organics were washed with water and brine, dried over $MgSO_4$, filtered and concentrated (aspirator). The α-branched acetonitrile was sufficiently pure for the next step and was carried on without purification.

The neat α-branched acetonitrile was poured into a 48 wt% solution of HBr in water and heated to reflux for 48 h. The solution was then cooled to rt and neutralized with NaOH. The solution was extracted with Et_2O. The combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated (aspirator) and the residue purified by flash chromatography (silica, 5 x 15 cm) with 10:1 hexanes/Et_2O as the eluent yielding known 3-isobutylbenzofuranone (1.484 g, 57%).[16]

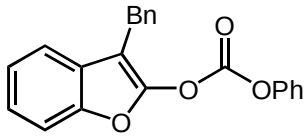
General Procedure for the synthesis of 3-alkyl benzofuranone enol carbonates 41: A solution of benzofuranone in THF (0.25 M) at 0 °C was treated with a slight excess of amine base and chloroformate. The resulting solution was allowed to stir at 0 °C for 30 min, then extracted from 0.1 M HCl with Et_2O. The combined organics were washed with brine, dried over $MgSO_4$, filtered and concentrated and the residues purified by flash chromatography using 10:1 hexanes/Et_2O as the eluent.

Representative procedure for the synthesis of 3-alkyl benzofuranone enol carbonates.

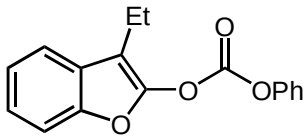


Carbonic acid 3-methyl-benzofuran-2-yl ester phenyl ester (41b). To a solution of the known 3-methyl-3*H*-benzofuran-2-one (100mg, 0.680 mmol) in THF (2.4 mL) was added Et_3N (0.14 mL, 1.02 mmol) at 0 °C. Phenyl chloroformate (0.13 mL, 1.02 mmol) was added to this solution which formed a precipitate and the resulting slurry was stirred at 0 °C for 30 min. The slurry was

poured into 0.1 M HCl and extracted with Et_2O. The combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated (aspirator). The residue was purified by flash chromatography (silica gel) using 10:1 hexane/Et_2O as the eluent, yielding pure *O*-carboxyl methylbenzofuranone **41b** as a clear, colorless oil (168 mg, 92%). Analytical tlc, 10:1 hexane/Et_2O, Rf= 0.30. Molecular ion calculated for $C_{16}H_{12}O_4$: 268.0736; [M^+], EIMS found m/z= 268.0739; IR (neat, cm^{-1}) 1795, C=O; 1223, C-O; 400 MHz NMR ($CDCl_3$, ppm) δ 7.48-7.39 (4 H, m) 7.31-7.22 (5 H, m) 2.18 (3 H, s). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 151.0, 150.4, 149.8, 149.3, 129.9, 129.6, 126.9, 124.4, 123.2, 120.8, 119.6, 111.2, 99.0, 6.8.

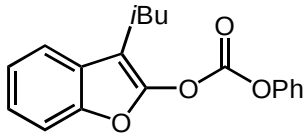


Carbonic acid 3-benzyl-benzofuran-2-yl ester phenyl ester (41c). Using the general procedure outlined above, the known 3-benzylbenzofuranone (0.691 g, 3.08 mmol) produced benzofuranone enol carbonate **41c** (0.700 g, 57%). Analytical tlc, 95:5 hexane/ether, Rf= 0.30. Molecular ion calculated for $C_{22}H_{16}O_4$: 344.10480 [M+]; EIMS found m/z= 344.1056, error= 2 ppm; IR (neat, cm^{-1}) 1791, C=O; 1187, C-O; 400 MHz ^1H NMR ($CDCl_3$, ppm) δ 7.42-7.14 (14 H, m) 4.00 (2 H, s). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 151.0, 150.2, 150.0, 138.4, 129.8, 128.8, 128.7, 126.9, 126.7, 124.5, 123.3, 120.8, 120.2, 111.3, 102.2, 24.5.



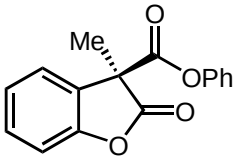
Carbonic acid 3-ethyl-benzofuran-2-yl ester phenyl ester (41d). Using the general procedure outlined above, the known 3-benzylbenzofuranone (0.500 g, 3.08 mmol) produced benzofuranone enol carbonate **41d** (0.644 g, 74%). Analytical tlc, 95:5 hexane/ether, Rf= 0.30. Molecular ion calculated for $C_{17}H_{14}O_4$: 282.08910 [M+]; EIMS found m/z= 282.0906, error= 5

ppm; IR (neat, cm^{-1}) 1793, C=O; 1214, C-O; 1167, C-O; 400 MHz ^{1}H NMR ($CDCl_3$, ppm) δ 7.52-7.20 (9 H, m) 2.65 (2 H, q, J= 5.3 Hz) 1.29 (3 H, t, J= 5.3 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 151.1, 150.4, 149.9, 148.8, 129.9, 128.8, 126.8, 124.2, 123.1, 120.8, 119.8, 104.7, 15.9, 13.3, 11.3.

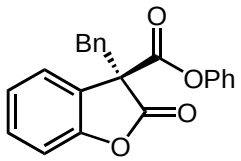


Carbonic acid 3-isobutyl-benzofuran-2-yl ester phenyl ester (41e). Using the general procedure outlined above, the known 3-benzylbenzofuranone (0.691g, 3.08 mmol) produced benzofuranone enol carbonate **41e** (0.659 g, 69%). Analytical tlc, 95:5 hexane/ether, Rf= 0.30. Molecular ion calculated for $C_{19}H_{18}O_4$: 310.12050 [M+]; EIMS found m/z= 310.1202, error= 1 ppm; IR (neat, cm^{-1}) 1794, C=O; 1208, C-O; 1164, C-O; 400 MHz ^{1}H NMR ($CDCl_3$, ppm) δ 7.51-7.21 (9 H, m) 2.53-2.50 (2 H, m) 2.11-2.00 (1 H, m) 0.98 (3 H, d, J= 7.6 Hz) 0.96 (3 H, d, J= 7.6 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 151.1, 150.4, 150.0, 149.8, 129.9, 129.3, 126.9, 124.2, 123.1, 120.8, 120.1, 111.3, 102.5, 31.6, 28.4, 22.8.

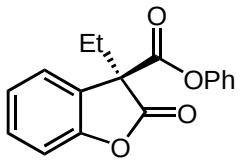
General Procedure for the carboxyl migration of 3-alkyl benzofuranone enol carbonates 41: A solution of benzofuranone enol carbonate (0.1 M) was treated with 1 mol% of (*R*)-TADMAP **1** at ambient temperature and allowed to stir until analytical TLC indicated all starting material had been consumed. The reaction was then quenched with iodomethane, and the solution concentrated (aspirator) and the residue filtered through a pad of silica with 1:1 hexanes/Et_2O as the eluent.



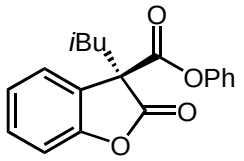
Representative procedure for the carboxyl migration of 3-alkyl benzofuranone enol carbonates. Carboxyl migration of 41b: Enol carbonate **41b** (13.4 mg, 0.050 mmol) and (*R*)-**1** (0.22 mg, 0.0005 mmol) were dissolved in Et_2O (0.5 mL) and allowed to stir for 4 h. The reaction was quenched with iodomethane (0.05 mL) The solution was then concentrated (N_2 stream), the residue was filtered through a silica plug with 1:1 hexane/Et_2O as the eluent, and concentrated (aspirator) yielding *C*-carboxyl methylbenzofuranone **42b** as a clear, colorless oil (12.3 mg, 92%, 92% ee). HPLC (Chiralcel OJ, 4.6mm x 25 cm, 90:10 hexane/isopropanol, 1.0 mL/min) T_R = 16.1 min (minor), T_R = 20.3 min (major). Analytical tlc, 5:1 hexane/Et_2O, Rf= 0.35. Molecular ion calculated for $C_{16}H_{12}O_4$: 268.0736; [M^+], EIMS found m/z= 268.0727; IR (neat, cm^{-1}) 1815, C=O; 1761, C=O; 1190, C-O; 500 MHz NMR ($CDCl_3$, ppm) δ 7.43-7.39 (2 H, m) 7.35-7.31 (2 H, m) 7.26-7.20 (3 H, m) 6.98-6.96 (2 H, m) 1.89 (3 H, s). ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 174.0, 167.0, 153.6, 150.4, 130.5, 129.7, 128.4, 126.7, 125.1, 123.6, 121.2, 111.6, 54.2, 20.8.



Carboxyl migration of enol carbonate 41c: Using the general procedure above enol carbonate **41c** (34 mg, 0.100 mmol) in Et_2O produced *C*-carboxyl benzylbenzofuranone **42c** (30 mg, 88%, 92% ee). HPLC (Chiralcel OJ, 4.6mm x 25 cm, 90:10 hexane/isopropanol, 1.0 mL/min) T_R = 36.7 min (minor), T_R = 46.2 min (major). Analytical tlc, 9:1 hexane/ether, Rf= 0.30. Molecular ion calculated for $C_{22}H_{16}O_4$: 344.10480 [M+]; EIMS found m/z= 344.1055, error= 2 ppm; IR (neat, cm^{-1}) 1806, C=O; 1758, C=O; 1181, C-O; 500 MHz ^1H NMR ($CDCl_3$, ppm) δ 7.48-6.96 (14 H, m) 3.73 (2 H, s). ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 172.6, 166.6, 153.8, 150.4, 133.5, 130.6, 130.3, 129.8, 128.5, 127.7, 126.8, 125.9, 124.8, 124.5, 121.3, 111.4, 60.5, 40.5.



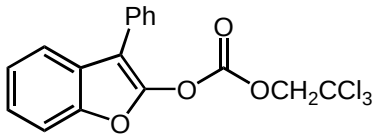
Carboxyl migration of enol carbonate 41d: Using the general procedure above enol carbonate **41d** (27 mg, 0.100 mmol) in Et_2O produced *C*-carboxyl ethylbenzofuranone **42d** (26 mg, 96%, 93% ee). HPLC (Chiralcel OJ, 4.6mm x 25 cm, 90:10 hexane/isopropanol, 1.0 mL/min) T_R = 22.8 min (minor), T_R = 29.7 min (major). Analytical tlc, 9:1 hexane/ether, Rf= 0.33. Molecular ion calculated for $C_{17}H_{14}O_4$: 282.08910 [M+]; EIMS found m/z= 282.0890, error= 1 ppm; IR (neat, cm^{-1}) 1810, C=O; 1756, C=O; 1185, C-O; 400 MHz ^{1}H NMR ($CDCl_3$, ppm) δ 7.40-7.16 (7 H, m) 6.97-6.93 (2 H, m) 2.50-2.31 (2 H, m) 0.84 (3H, d, J=5.6 Hz) 0.81 (3 H, d, J= 5.6 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 172.9, 166.7, 154.1, 150.5, 130.4, 129.6, 126.5, 126.4, 124.9, 123.9, 121.2, 111.3, 59.4, 28.3, 11.3.



Carboxyl migration of enol carbonate 41e: Using the general procedure above enol carbonate **41e** (31 mg, 0.100 mmol) in Et_2O produced *C*-carboxyl isobutylbenzofuranone **42e** (30 mg, 97%, 93% ee). HPLC (Chiralcel OJ, 4.6mm x 25 cm, 90:10 hexane/isopropanol, 1.0 mL/min) T_R = 12.0 min (minor), T_R = 17.8 min (major). Analytical tlc, 9:1 hexane/ether, Rf= 0.33. Molecular ion calcuated for $C_{19}H_{18}O_4$: 310.12050 [M+]; found m/z= 310.1206, error= 0 ppm; IR (neat, cm^{-1}) 1808, C=O; 1760, C=O; 1185, C-O; 500 MHz ^{1}H NMR ($CDCl_3$, ppm) δ 7.45-7.26 (7 H, m) 6.99-6.97 (2 H, m) 2.49-2.39 (2 H, m) 1.64-1.56 (1 H, m) 0.89-0.79 (6 H, m). ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 173.6, 167.1, 153.9, 150.4, 130.4, 129.7, 126.7, 124.9, 124.4, 121.2, 111.6, 58.4, 42.4, 25.2, 24.1, 22.9.

3-Phenyl Benzofuranone Enol Carbonate Synthesis & Migration

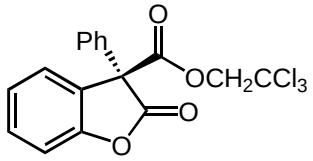
Enol carbonates **39a-c,e**[18,19] were prepared according to literature precedent. Enol carbonate **39d** was prepared analogously as detailed below.



Carbonic acid 3-phenyl-benzofuran-2-yl ester 2,2,2-trichloroethyl ester (39d). To a solution of the known 3-phenyl-3*H*-benzofuran-2-one[20] (250 mg, 1.19 mmol) in THF (4 mL) was added *i*Pr_2EtN (0.23 mL, 1.32 mmol, Aldrich) at 0 °C. 2,2,2-Trichloroethyl chloroformate (0.17 mL, 1.23 mmol) was added to this solution which formed a precipitate and the resulting slurry was stirred at 0 °C for 30 min. The slurry was poured into 0.1 M HCl and extracted with Et_2O. The combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated (aspirator). The residue was purified by flash chromatography (silica gel) using 95:5 hexane/Et_2O as the eluent, yielding pure *O*-acyl phenylbenzofuranone **39d** as a clear, colorless oil (389 mg, 85%). Analytical tlc, 95:5 hexane/Et_2O, Rf= 0.32. Molecular ion calculated for $C_{17}H_{11}Cl_3O_4$: 383.9723; [M^+], EIMS found m/z= 383.9728; IR (neat, cm^{-1}) 1790, C=O; 1182, C-O; 500 MHz NMR ($CDCl_3$, ppm) δ 7.72-7.70 (1 H, m) 7.61-7.59 (2 H, m) 7.47-7.42 (3 H, m) 7.35-7.26 (3 H, m) 4.82 (2 H, s). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 151.0, 150.0, 148.5, 129.9, 129.3, 128.4, 128.0, 127.6, 125.1, 124.0, 120.7, 111.7, 105.4, 93.8, 78.0.

General procedure for 3-phenyl benzofuranone enol carbonate carboxyl migration:

A solution of benzofuranone enol carbonate **39** (0.1 M) was treated with TADMAP at room temperature unless otherwise specified and the reaction monitored (when possible) by analytical TLC. When the reaction showed no remaining starting material, the reaction was quenched with iodomethane and the solution concentrated (aspirator). The residue was taken up in Et_2O and filtered through a silica plug to provide pure material.



Carboxyl migration of 39d: A solution of **39d** (38 mg, 0.100 mmol) and (*R*)-**1** (8.7 mg, 0.020 mmol) was prepared in CH_2Cl_2 (1 mL) at –78 °C and allowed to warm to – 40 °C, and stirring was continued for 18 h at –40 °C. The solution was allowed to warm to rt, then concentrated (N_2 stream). The residue was purified by flash chromatography (silica gel, 15 x 1.5 cm column) with 2:1 EtOAc/hexane as the eluent. After elution with 200 mL, solvent was switched to pure EtOAc and elution continued for another 200 mL. The first compound eluted within the first 80 mL and these fractions were concentrated (aspirator) yielding *C*-carboxyl methylbenzofuranone **40d** as a clear, colorless oil (35 mg, 92%, 86% ee). HPLC (Regis Whelk-O, 4.6mm x 25 cm, 98:2 hexane/isopropanol, 1.0 mL/min) T_R = 11.9 min (major), T_R = 15.2 min (minor). Analytical tlc, 1:1 hexane/Et_2O, Rf= 0.50. Molecular ion calculated for $C_{17}H_{11}Cl_3O_4$: 383.9723; [M^+], EIMS found m/z= 383.9721; IR (neat, cm^{-1}) 1814, C=O; 1758, C=O; 1196, C-O; 500 MHz NMR ($CDCl_3$, ppm) δ 7.62-7.60 (1 H, m) 7.52-7.48 (1 H, m) 7.45-7.39 (5 H, m) 7.34-7.30 (1 H, m) 7.27-7.25 (1 H, m) 4.85-4.80 (2 H, m). ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 170.9, 166.3, 154.0, 133.7, 131.2, 129.4, 129.2, 127.9, 127.0, 125.0, 124.7, 111.7, 94.2, 75.1, 62.5. A second compound began eluting from the column after 200 mL of solvent had passed and fractions containing this compound were concentrated to yield TADMAP **1** (8.3 mg, 95% recovery).

C-Carboxyl benzofuranones **40a-c**[18] and **40e**[19] are known compounds.

HPLC data for migration product 40a: HPLC (Whelk-O, 4.6mm x 25 cm, 90:10 hexane/isopropanol, 1.0 mL/min) T_R = 12.5 min (major), T_R = 14.1 min (minor).

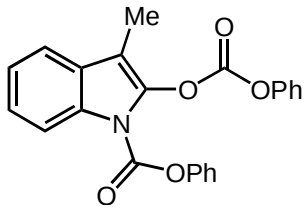
HPLC data for migration product 40b: HPLC (Chiralcel OJ, 4.6mm x 25 cm, 90:10 hexane/isopropanol, 1.0 mL/min) T_R = 16.9 min (major), T_R = 35.5 min (minor).

HPLC data for migration product 40c: HPLC (Regis Whelk-O, 4.6mm x 25 cm, 98:2 hexane/isopropanol, 1.0 mL/min) T_R = 13.6 min (major), T_R = 15.7 min (minor).

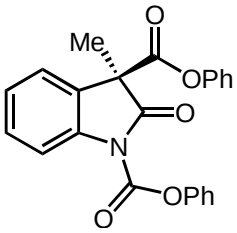
HPLC data for migration product 40e: HPLC (Regis Whelk-O, 4.6mm x 25 cm, 98:2 hexane/isopropanol, 1.0 mL/min) T_R = 9.3 min (major), T_R = 10.5 min (minor). Absolute stereochemistry assigned by previously reported optical rotation data.[19] The other 3-phenyl benzofuranone products were assigned by analogy.

Synthesis of 3-Alkyl Oxindole Enol Carbonates

3-Methyloxindole 47 (R = H): The known oxindole was prepared according to the method of Takase and coworkers.[21] 3-Methylindole (1.31 g, 9.99 mmol, Aldrich, CAUTION: STENCH!) was dissolved in DMSO (7.1 mL, 100.1 mmol, Aldrich). To this solution was added aq HCl (12M, 15 mL). After 15 min, the reaction was extracted from water with EtOAc. The combined organics were washed with brine, dried over $MgSO_4$, filtered through a plug of silica and concentrated (aspirator) yielding oxindole **47** (R = H) as a white solid (0.933 g, 64%). The material was sufficiently pure for subsequent reactions, therefore was carried on without purification.



***N,O*-bis(phenoxycarbonyl) oxindole enol carbonate 49a:** The known 3-methyloxindole[21] **47** (R = H) (0.578 g, 3.523 mmol) was dissolved in THF (11 mL). To this solution was added Et_3N (1.1 mL, 7.75 mmol) and phenyl chloroformate (1.75 mL, 7.75 mmol, Aldrich). After 30 min at room temperature, this solution was extracted from 0.1 M HCl with Et_2O. The combined organics were washed with brine, dried over $MgSO_4$, filtered and concentrated (aspirator). The residue was purified by flash chromatography (silica, 5 x 15 cm) with 88:12 hexanes/Et_2O as the eluent yielding oxindole enol carbonate **49a** (0.954 g, 70%). After flash chromatography (silica, 5 x 15 cm, 88:12 hexanes/Et_2O) the material was sufficiently pure for carboxyl migration reactions. Analytical tlc, 7:1 hexane/Et_2O, Rf= 0.35. Molecular ion calculated for $C_{23}H_{17}NO_5$: 387.11067; [M^+], EIMS found m/z= 387.1103; IR (neat, cm^{-1}) 1788, C=O; 1746, C=O; 500 MHz NMR ($CDCl_3$, ppm) δ 8.25 (1 H, d, J= 8.3) 7.60-7.19 (13 H, m) 2.34 (3 H, s). ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 151.5, 151.2, 150.3, 148.9, 137.5, 132.5, 130.2, 129.9, 128.4, 126.9, 125.5, 124.1, 121.9, 121.1, 119.4, 115.9, 106.7, 7.4.

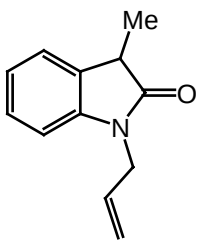


Carboxyl Migration Reaction of *N,O*-bis(phenoxycarbonyl) enol carbonate 50a. To a 0.1 M solution of enol carbonate **49a** (~0.025 mmol) was added 10 mol% of TADMAP **1** and the reaction was sealed in a screw-top vial. The reaction was monitored by analytical TLC and quenched with iodomethane when all starting material had been consumed. The solution was

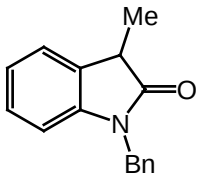
then concentrated and the crude compound **50a** was analyzed directly by analytical HPLC on chiral support. HPLC (Chiralcel AD, 4.6mm x 25 cm, 90:10 hexane/isopropanol, 1.0 mL/min) T_R = 9.9 min (minor), T_R = 14.0 min (major). Analytical tlc, 1:1 hexane/Et_2O, Rf= 0.50. Molecular ion calculated for $C_{23}H_{17}NO_5$: 387.11067; [M^+], EIMS found m/z= 387.1102; IR (neat, cm^{-1}) 1746, C=O; 1185, C-O; 500 MHz NMR ($CDCl_3$, ppm) δ 8.10 (1 H, d, J= 7.7 Hz) 7.50-7.46 (4 H, m) 7.38-7.32 (6 H, m) 7.26-7.23 (1 H, m) 7.02-7.01 (2 H, m) 1.94 (3 H, s). ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 172.6, 167.8, 150.6, 150.3, 149.5, 139.4, 130.1, 129.9, 129.7, 128.9, 126.8, 126.6, 125.9, 123.2, 121.7, 116.2, 56.2, 21.1.

General procedure for the synthesis of 1-alkyl-3-methyl oxindoles: To a slurry of NaH (3 eq) in DMF (1.7 M) was added a solution of 3-methylindole (Aldrich, CAUTION: STENCH!) as a solution in DMF (~1.25 M). The solution was stirred at rt for 1 h, then cooled to 0 °C and treated with an alkylating agent (1.3 eq). The resulting solution was allowed to warm to rt and stir overnight. The solution was then poured into sat aq NH_4Cl and extracted with Et_2O. The combined organics were washed with brine, dried over $MgSO_4$, filtered and concentrated (aspirator). The resulting N-alkyl compound was used without purification.

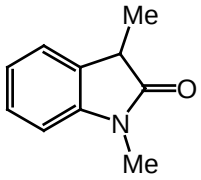
The *N*-alkyl 3-methylindole was dissolved in DMSO (0.6 M) and treated with conc HCl (twice the volume of DMSO). The reaction was then monitored by analytical TLC. When all of the starting material has been consumed, the solution is extracted from water with EtOAc. The combined organics were then washed with brine, dried over $MgSO_4$, filtered and concentrated (aspirator). The residue was purified by flash chromatography.



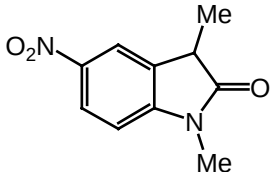
1-Allyl-3-methyloxindole: Using the general procedure outlined above, 3-methylindole (0.385 g, 2.94 mmol, Aldrich) yielded the known oxindole[22] (0.228 g, 41% yield over two steps). The material was purified by flash chromatography (silica, 3 x 15 cm) with 88:12 hexanes/Et_2O as the eluent.



1-Benzyl-3-methyloxindole: Using the general procedure outlined above, 3-methylindole (2.8 g, 21.3 mmol, Aldrich) yielded the known oxindole[23] (1.522 g, 30% yield over two steps). The material was purified by flash chromatography (silica, 3 x 15 cm) with 60:40 hexanes/Et_2O as the eluent.



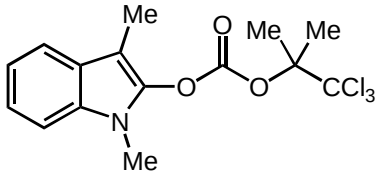
1-Methyl-3-methyloxindole: Using the general procedure outlined above, 3-methylindole (2.8 g, 21.3 mmol, Aldrich) yielded the known oxindole[24] (2.283 g, 66% yield over two steps). The material was purified by flash chromatography (silica, 3 x 15 cm) with 40:60 hexanes/Et_2O as the eluent.



1-Methyl-3-methyl-5-nitrooxindole: The known 1-methyl-3-methyl-5-nitroindole[25] was prepared according to literature precedent. Treatment of indole (0.653 g, 3.433 mmol) with DMSO (10 mL) and conc HCl (22 mL) at 50 °C for 4 h completely consumed the starting

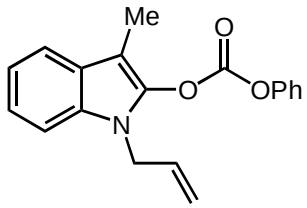
material. The solution was extracted from water with EtOAc, and the combined organics washed with brine, dried over $MgSO_4$, filtered and concentrated (aspirator). The residue was purified by flash chromatography (silica, 3 x 15 cm) with 96:4 CH_2Cl_2/AcOH as the eluent yielding oxindole (0.220 g, 31%).

General Procedure for the Synthesis of 1-alkyl-3-methyl oxindole enol carbonates (49b-h): To a solution of KHMDS in THF (1.2 eq, ~1.0 M) at –78 °C was added a solution of oxindole in THF (0.5 M). This solution was allowed to stir at –78 °C, then transferred to a solution of chloroformate in THF (1.2 eq, 0.6 M) at –78 °C. This solution was allowed to warm to rt, then extracted from 0.1 M HCl by Et_2O. The combined organics were washed with brine, dried over $MgSO_4$, filtered and concentrated (aspirator). The residue was purified by flash chromatography.

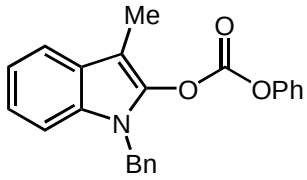


Representative Procedure of the Synthesis of 1-alkyl-3-methyl oxindole enol carbonates. Carbonic acid 1,3-dimethyl-1*H*-indol-2-yl ester 2,2,2-trichloro-1,1-dimethylethyl ester 49h. A solution of the known 1,3-dimethyl-1,3-dihydro-indol-2-one[24] (0.500 g, 3.10 mmol) in THF (4 mL) was added slowly to a solution of KHMDS (0.743 g, 3.72 mmol, Aldrich) in THF (4 mL) at –78 °C. The solution was stirred at –78 °C for 30 min, then transferred via cannula to a solution of 2,2,2-trichloro-1,1-dimethylethyl chloroformate (0.893 g, 3.72 mmol, Aldrich) in THF (5 mL) at –78 °C. The solution was allowed to warm to rt, then poured into 0.1 M HCl, and extracted with Et_2O. The combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated (aspirator). The residue was purified by flash chromatography (silica gel) with 9:1 hexane/Et_2O as the eluent, yielding the known,[19] pure **49h** as a white crystalline solid (940 mg, 83%). Analytical tlc, 1:1 hexane/Et_2O, Rf= 0.73. Molecular ion calculated for $C_{15}H_{16}Cl_3NO_3$:

363.0196; [M^+], EIMS found m/z= 363.1082; IR (neat, cm^{-1}) 1774, C=O; 1238, C-O; 1143, C-O; 400 MHz NMR ($CDCl_3$, ppm) δ 7.58 (1 H, d, J= 8.1 Hz) 7.30-7.17 (3 H, m) 3.61 (3 H, s) 2.26 (3 H, s) 2.07 (6 H, s). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 149.9, 139.3, 132.9, 126.6, 121.1, 119.8, 119.1, 109.1, 105.1, 96.7, 91.7, 28.5, 21.4, 7.6.

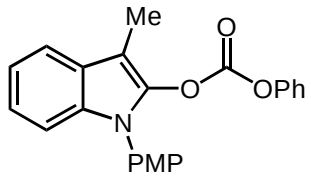


Carbonic acid 1-allyl-3-methyl-1*H*-indol-2-yl ester phenyl ester 49b. Using the general procedure outlined above, 1-allyl-3-methyl-1,3-dihydro-indol-2-one (0.285 g, 1.522 mmol) yielded enol carbonate **49b** (0.232 g, 50%) after purification by flash chromatography (silica, 5 x 15 cm, 75:25 hexanes/Et_2O). The material was sufficiently pure for the screening of carboxyl migration reaction conditions. Analytical tlc, 9:1 hexane/Et_2O, Rf= 0.25. Molecular ion calculated for $C_{19}H_{17}NO_3$: 307.1208; [M^+], EIMS found m/z= 307.1200; IR (neat, cm^{-1}) 1787, C=O; 1194, C-O; 1179, C-O; 500 MHz NMR ($CDCl_3$, ppm) δ 7.66 (1 H, d, J= 7.8 Hz) 7.52-7.49 (2 H, m) 7.37-7.24 (6 H, s) 6.06-6.00 (1 H, m) 5.28-5.19 (2 H, m) 4.76 (2 H, d, J= 4.9 Hz) 2.37 (3 H, s). ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 151.0, 150.8, 138.8, 133.1, 132.2, 129.8, 126.7, 121.9, 120.7, 119.8, 119.1, 117.0, 109.4, 97.2, 44.8, 7.5.



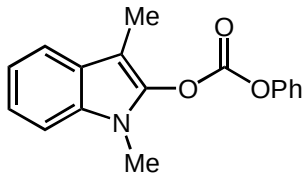
Carbonic acid 1-benzyl-3-methyl-1*H*-indol-2-yl ester phenyl ester 49c. Using the general procedure outlined above, 1-benzyl-3-methyl-1,3-dihydro-indol-2-one (0.557 g, 2.347 mmol) yielded enol carbonate **49c** (0.391 g, 46%) after purification by flash chromatography (silica, 5 x

15 cm, 75:25 hexanes/Et_2O). The material was sufficiently pure for the screening of carboxyl migration reaction conditions. Analytical tlc, 9:1 hexane/Et_2O, Rf= 0.25. Molecular ion calculated for $C_{23}H_{19}NO_3$: 357.13649; [M^+], EIMS found m/z= 357.1353; IR (neat, cm^{-1}) 1786, C=O; 1187, C-O; 1179, C-O; 500 MHz NMR ($CDCl_3$, ppm) δ 7.55 (1 H, d, J= 6.7 Hz) 7.32-7.04 (13 H, m) 5.21 (2 H, s) 2.26 (3 H, s). ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 150.9, 150.6, 139.0, 137.3, 132.4, 129.7, 128.9, 127.7, 126.8, 126.6, 122.1, 120.7, 119.9, 119.1, 109.6, 97.5, 46.1, 7.6.



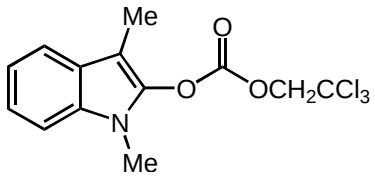
Carbonic acid 1-(4-methoxyphenyl)-3-methyl-1*H*-indol-2-yl ester phenyl ester 49d. Analogous to the procedure of Klapars and Buchwald, 1-(4'-methoxyphenyl)-3-methylindole was prepared.[26] 3-Methylindole (0.754 g, 5.76 mmol, Aldrich) was combined with 4-methoxyphenyl iodide (1.6 g, 6.91 mmol, Aldrich), Cu(I)I (55 mg, 0.29 mmol, Aldrich), *N*,*N*'-dimethylethylenediamine (0.12 mL, 1.15 mmol, Aldrich) and K_3PO_4 (2.6 g) under an inert atmosphere. The solids were taken up in toluene (6 mL) and heated to 110 °C for 2 days. The solution was then cooled to rt, and extracted from water with Et_2O. The combined organics were washed with 0.1 M HCl and brine, dried over $MgSO_4$, filtered and concentrated (aspirator). The residue was purified by flash chromatography (silica, 5 x 15 cm) with 95:5 hexanes/Et_2O as the eluent yielding 1-(4'-methoxyphenyl)-3-methylindole (0.795 g, 58%) as a white solid. This material was taken up in DMSO (5 mL) and treated with conc HCl at 45 °C for 1 day. The solution was then extracted from water with EtOAc, the combined organics washed with brine, dried over $MgSO_4$, filtered and concentrated (aspirator). The residue was purified by flash chromatography (silica, 5 x 15 cm) with 1:1 hexanes/Et_2O as the eluent yielding the corresponding oxindole (0.458 g, 54%). This material was dissolved in THF (3 mL) and added to

a solution of KHMDS (0.435 g, 2.18 mmol, Aldrich) in THF (3 mL) at –78 °C. This solution was allowed to stir at –78 °C for 30 min then transferred via cannula to a solution of phenyl chloroformate (0.29 mL, 2.31 mmol, Aldrich) in THF (3 mL) at –78 °C. This solution was allowed to warm to rt, then extracted from 0.1 M HCl with Et_2O. The combined organics were washed with brine, dried over $MgSO_4$, filtered and concentrated (aspirator). The residue was purified via flash chromatography (silica, 3 x 15 cm) with 88:12 hexanes/Et_2O as the eluent yielding enol carbonate **49d** (0.330 g, 30% over two steps from 1-(4'-methoxyphenyl)-3-methylindole) as a white solid. Analytical tlc, 1:1 hexane/Et_2O, Rf= 0.50. Molecular ion calculated for $C_{23}H_{19}NO_4$: 373.13141; [M^+], EIMS found m/z= 373.1315; IR (neat, cm^{-1}) 1785, C=O; 1196, C-O; 500 MHz NMR ($CDCl_3$, ppm) δ 7.62-7.60 (1 H, m) 7.39-7.36 (4 H, m) 7.27-7.24 (1 H, m) 7.21-7.19 (3 H, m) 7.08-7.03 (4 H, m) 3.91 (3 H, s) 2.34 (3 H, s). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 159.3, 150.9, 133.7, 129.7, 128.8, 128.4, 126.7, 122.5, 120.9, 120.7, 120.4, 119.1, 114.9, 110.2, 98.1, 55.8, 7.4.

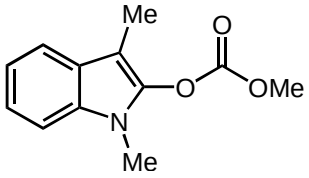


Carbonic acid 1-methyl-3-methyl-1*H*-indol-2-yl ester phenyl ester 49e. Using the general procedure outlined above, 1,3-dimethyl-1,3-dihydro-indol-2-one (0.500 g, 3.102 mmol) yielded enol carbonate **49e** (0.522 g, 63%) after purification by flash chromatography (silica, 5 x 15 cm, 60:40 hexanes/Et_2O). The material was sufficiently pure for the screening of carboxyl migration reaction conditions. Analytical tlc, 6:4 hexane/Et_2O, Rf= 0.30. Molecular ion calculated for $C_{17}H_{15}NO_3$: 281.10519; [M^+], EIMS found m/z= 281.1054; IR (neat, cm^{-1}) 1783, C=O; 1184, C-O; 1003, C-O; 500 MHz NMR ($CDCl_3$, ppm) δ 7.62 (1 H, d, J= 7.8 Hz) 7.51-7.48 (2 H, m)

7.39-7.21 (6 H, m) 3.71 (3 H, s) 2.34 (3 H, s). ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 151.2, 139.3, 132.9, 130.0, 126.9, 126.7, 122.0, 120.9, 119.8, 119.2, 109.2, 96.9, 28.7, 7.7.

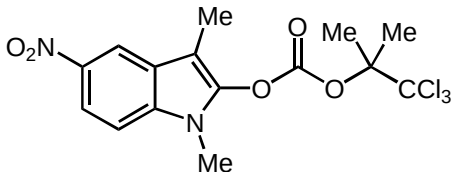


Carbonic acid 1-methyl-3-methyl-1*H*-indol-2-yl ester (2,2,2-trichloroethyl) ester 49g. Using the general procedure outlined above, 1,3-dimethyl-1,3-dihydro-indol-2-one (0.500 g, 3.102 mmol) yielded enol carbonate **49g** (0.578 g, 55%) after purification by flash chromatography (silica, 5 x 15 cm, 88:12 hexanes/Et_2O). The material was sufficiently pure for the screening of carboxyl migration reaction conditions. Analytical tlc, 85:15 hexane/Et_2O, Rf= 0.50. Molecular ion calculated for $C_{13}H_{12}NO_3Cl_3$: 334.98827; [M^+], EIMS found m/z= 334.9882; IR (neat, cm^{-1}) 1782, C=O; 1202, C-O; 400 MHz NMR ($CDCl_3$, ppm) δ 7.53 (1 H, d, J= 8.0 Hz) 7.23-7.11 (3 H, m) 4.93 (2 H, s) 3.56 (3 H, s) 2.20 (3 H, s). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 152.0, 138.9, 132.8, 126.5, 122.1, 119.8, 119.2, 109.1, 96.9, 94.3, 77.7, 28.5, 7.4.



Carbonic acid 1-methyl-3-methyl-1*H*-indol-2-yl ester methyl ester 49f. Using the general procedure outlined above, 1,3-dimethyl-1,3-dihydro-indol-2-one (1.242 g, 7.70 mmol) yielded enol carbonate **49f** (0.833 g, 49%) after purification by flash chromatography (silica, 5 x 15 cm, 80:20 hexanes/Et_2O). The material was sufficiently pure for the screening of carboxyl migration reaction conditions. Analytical tlc, 85:15 hexane/Et_2O, Rf= 0.25. Molecular ion calculated for $C_{12}H_{13}NO_3$: 219.08954; [M^+], EIMS found m/z= 219.0895; IR (neat, cm^{-1}) 1771, C=O; 1237, C-O; 1206, C-O; 400 MHz NMR ($CDCl_3$, ppm) δ 7.51-7.49 (1 H, m) 7.22-7.08 (3 H, m) 3.95 (3

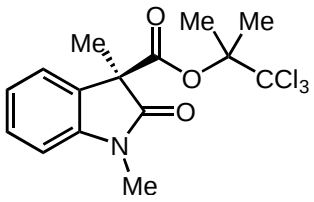
H, s) 3.55 (3 H, s) 2.17 (3 H, s). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 153.1, 132.5, 126.3, 121.6, 121.5, 119.6, 119.4, 118.8, 108.8, 96.3, 56.1, 28.2, 7.2.



Carbonic acid 1-methyl-3-methyl-5-nitro-1*H*-indol-2-yl ester (2,2,2-trichloro-1,1-dimethylethyl) ester 53. Using the general procedure outlined above, 1,3-dimethyl-5-nitro-1,3-dihydro-indol-2-one (0.171 g, 0.829 mmol) yielded enol carbonate **53** (0.273 g, 81%) after purification by flash chromatography (silica, 3 x 15 cm, 80:20 hexanes/Et_2O). The material was sufficiently pure for the screening of carboxyl migration reaction conditions. Analytical tlc, 1:1 hexane/Et_2O, Rf= 0.50. Molecular ion calculated for $C_{15}H_{15}N_2O_5Cl_3$: 408.004655; [M^+], EIMS found m/z= 408.0062; IR (neat, cm^{-1}) 1773, C=O; 1152, C-O; 1100, C-O; 500 MHz NMR ($CDCl_3$, ppm) δ 8.51 (1 H, d, J= 1.9 Hz) 8.16-8.13 (1 H, m) 7.29-7.27 (1 H, m) 3.67 (3 H, s) 2.26 (3 H, s) 2.05 (6 H, s). ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 149.0, 141.6, 141.0, 135.5, 125.7, 117.4, 116.2, 108.9, 99.5, 92.1, 28.8, 21.1, 7.3.

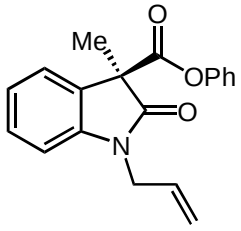
Carboxyl Migration of 3-Alkyl Oxindole Enol Carbonates

General Procedure for the Carboxyl Migration of 3-Alkyloxindole enol carbonates: To a 0.1 M solution of enol carbonate (~0.025 mmol unless otherwise stated) was added 10 mol% of TADMAP **1** and the reaction was sealed in a screw-top vial. The reaction was monitored by analytical TLC and quenched with iodomethane when all starting material had been consumed. The solution was then concentrated and the crude compound was analyzed directly by analytical HPLC on chiral support.



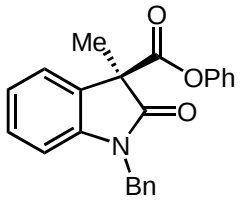
Representative Procedure for the Carboxyl Migration of 3-Alkyloxindole enol carbonates:

Carboxyl migration of 49h. A solution of (*S*)-**1** (1.1 mg, 0.0025 mmol) in *t*-amyl alcohol (0.3 mL) was added to **49h** (9 mg, 0.025 mmol). After 24 h, the solution was concentrated (N_2 stream). The crude residue was mostly **50h** (49% ee), as ascertained by NMR. HPLC (Chiralcel OD, 4.6mm x 25 cm, 90:10 hexane/isopropanol, 1.0 mL/min) T_R = 7.4 min (minor), T_R = 9.1 min (major). Analytical tlc, 1:1 hexane/Et_2O, Rf= 0.50. Molecular ion calculated for $C_{15}H_{16}Cl_3NO_3$: 363.0196; [M^+], EIMS found m/z= 363.1097; IR (neat, cm^{-1}) 1749, C=O; 1715, C=O; 1119, C-O; 500 MHz NMR ($CDCl_3$, ppm) δ 7.32-7.25 (2 H, m) 7.07-7.04 (1 H, m) 6.86-6.84 (1 H, m) 3.23 (3 H, s) 1.85 (3 H, s) 1.71 (3 H, s) 1.66 (3 H, s). ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 174.8, 167.5, 144.3, 130.0, 129.4, 123.0, 122.8, 108.7, 105.7, 89.8, 56.3, 26.7, 21.4, 20.9, 18.5. The absolute stereochemistry of this compound was identified by comparison of the sign of optical rotation with the literature value[19] and all other *C*-carboxylated oxindole products were assigned by analogy.

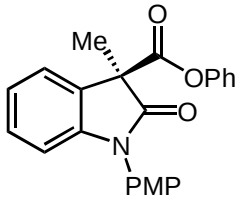


HPLC data for migration product 50b: HPLC (Chiralcel AD, 4.6mm x 25 cm, 90:10 hexane/isopropanol, 1.0 mL/min) T_R = 8.5 min (minor), T_R = 9.9 min (major). Analytical tlc, 1:1 hexane/Et_2O, Rf= 0.25. Molecular ion calculated for $C_{19}H_{17}NO_3$: 307.120844; [M^+], EIMS found m/z= 307.1211; IR (neat, cm^{-1}) 1756, C=O; 1713, C=O; 1181, C-O; 400 MHz NMR ($CDCl_3$,

ppm) δ 7.38-6.84 (9 H, m) 5.88-5.79 (1 H, m) 5.24-5.16 (2 H, m) 4.50-4.27 (2 H, m) 1.76 (3 H, s). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 174.4, 168.3, 150.4, 142.9, 130.7, 129.3, 129.2, 126.0, 123.0, 121.1, 117.3, 109.5, 55.1, 42.3, 19.8.

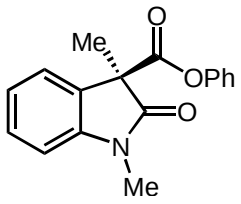


HPLC data for migration product 50c: HPLC (Chiralcel AD, 4.6mm x 25 cm, 90:10 hexane/isopropanol, 1.0 mL/min) T_R = 15.1 min (major), T_R = 29.7 min (minor). Analytical tlc, 1:1 hexane/Et_2O, Rf= 0.25. Molecular ion calculated for $C_{23}H_{19}NO_3$: 357.13649; [M^+], EIMS found m/z= 357.1360; IR (neat, cm^{-1}) 1756, C=O; 1713, C=O; 1189, C-O; 500 MHz NMR ($CDCl_3$, ppm) δ 7.40-7.21 (10 H, m) 7.13-7.10 (1 H, m) 7.02-7.00 (1 H, m) 6.79 (1 H, d, J= 7.8 Hz) 5.19 (1 H, d, J= 5.4 Hz) 4.87 (1 H, d, J= 5.4 Hz) 1.87 (3 H, s). ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 174.9, 168.3, 150.5, 142.9, 135.4, 129.8, 129.4, 129.3, 128.8, 127.7, 127.1, 126.1, 123.1, 123.0, 121.2, 109.8, 55.3, 43.9, 19.8.

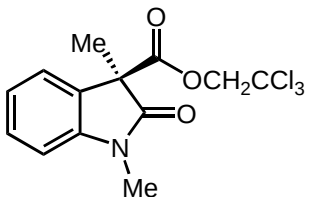


HPLC data for migration product 50d: HPLC (Chiralcel OD, 4.6mm x 25 cm, 90:10 hexane/isopropanol, 1.0 mL/min) T_R = 9.1 min (major), T_R = 14.3 min (minor). Analytical tlc, 1:1 hexane/Et_2O, Rf= 0.25. Molecular ion calculated for $C_{23}H_{19}NO_4$: 373.13141; [M^+], EIMS found m/z= 373.1320; IR (neat, cm^{-1}) 1760, C=O; 1723, C=O; 1189, C-O; 500 MHz NMR ($CDCl_3$, ppm) δ 7.43-7.00 (12 H, m) 6.84 (1 H, d, J= 7.8 Hz) 3.88 (3 H, s) 1.89 (3 H, s). ^{13}C

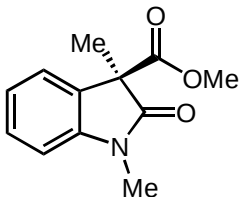
NMR (126 MHz, $CDCl_3$, ppm) δ 174.4, 168.4, 159.4, 150.5, 144.3, 129.5, 129.4, 129.2, 128.0, 126.7, 126.1, 123.4, 123.1, 121.2,109.9, 55.6, 19.9.



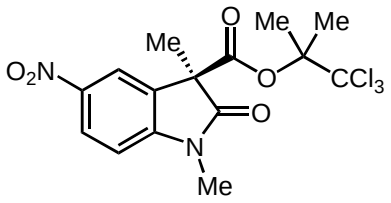
HPLC data for migration product 50e: HPLC (Chiralcel AD, 4.6mm x 25 cm, 90:10 hexane/isopropanol, 1.0 mL/min) T_R = 9.1 min (major), T_R = 13.0 min (minor). Analytical tlc, 1:1 hexane/Et_2O, Rf= 0.25. Molecular ion calculated for $C_{17}H_{15}NO_3$: 281.10519; [M^+], EIMS found m/z= 281.1058; IR (neat, cm^{-1}) 1756, C=O; 1715, C=O; 1187, C-O; 500 MHz NMR ($CDCl_3$, ppm) δ 7.38-7.28 (4 H, m) 7.19-7.11 (2 H, m) 6.95-6.90 (3 H, m) 3.29 (3 H, s) 1.77 (3 H, s). ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 174.9, 168.7, 150.7, 144.1, 130.0, 129.6, 126.3, 123.2, 121.5, 108.9, 55.4, 26.9, 20.2.



HPLC data for migration product 50g: HPLC (Chiralcel OD, 4.6mm x 25 cm, 90:10 hexane/isopropanol, 1.0 mL/min) T_R = 7.6 min (major), T_R = 10.0 min (minor). Analytical tlc, 6:4 hexane/Et_2O, Rf= 0.25. Molecular ion calculated for $C_{13}H_{12}NO_3Cl_3$: 334.98828; [M^+], EIMS found m/z= 334.9896; IR (neat, cm^{-1}) 1758, C=O; 1719, C=O; 1119, C-O; 500 MHz NMR ($CDCl_3$, ppm) δ 7.37-7.30 (2 H, m) 7.10-7.07 (1 H, m) 6.90-6.89 (1 H, m) 4.80 (1 H, d, J= 12.2 Hz) 4.61 (1 H, d, J= 12.2 Hz) 3.28 (3 H, s) 1.76 (3 H, s). ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 174.2, 168.1, 143.8, 129.4, 129.1, 123.4, 122.9, 108.5, 74.3, 55.0, 26.6, 19.4.



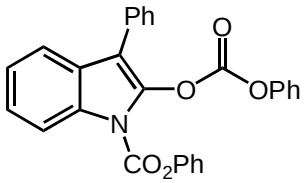
HPLC data for migration product 40f: HPLC (Chiralcel OD, 4.6mm x 25 cm, 90:10 hexane/isopropanol, 1.0 mL/min) T_R = 8.0 min, T_R = 9.7 min. Analytical tlc, 1:1 hexane/Et_2O, Rf= 0.25. Molecular ion calculated for $C_{12}H_{13}NO_3$: 219.08954; [M^+], EIMS found m/z= 219.0891; IR (neat, cm^{-1}) 1740, C=O; 1714, C=O; 1104, C-O; 500 MHz NMR ($CDCl_3$, ppm) δ 7.34-7.31 (1 H, m) 7.27-7.25 (1 H, m) 7.08-7.05 (1 H, m) 6.87 (1 H, d, J= 7.8 Hz) 3.65 (3 H, s) 3.25 (3 H, s) 1.67 (3 H, s). ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 175.1, 170.2, 143.6, 130.0, 129.0, 123.0, 122.9, 108.5, 54.9, 53.0, 26.5, 20.2.



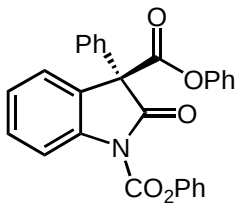
Carboxyl migration of enol carbonate 53: A solution of (*S*)-**1** (2.2 mg, 0.005 mmol) in CH_2Cl_2 (0.5 mL) was added to **53** (20 mg, 0.050 mmol) at 0 °C. After 24 h, the solution was quenched with iodomethane (0.10 mL), filtered through a plug of silica and concentrated (N_2 stream) yielding **54** (20 mg, quantitative, 75% ee). HPLC (Chiralcel OJ, 4.6mm x 25 cm, 90:10 hexane/isopropanol, 1.0 mL/min) T_R = 20.7 min (minor), T_R = 28.8 min (major). Analytical tlc, 4:6 hexane/Et_2O, Rf= 0.35. Molecular ion calculated for $C_{15}H_{15}N_2O_5Cl_3$: 408.00466; [M^+], EIMS found m/z= 408.0048; IR (neat, cm^{-1}) 1758, C=O; 1731, C=O; 1111, C-O; 500 MHz NMR ($CDCl_3$, ppm) δ 8.32-8.30 (1 H, m) 8.18 (1 H, d, J= 2.5 Hz) 6.94 (1 H, d, J= 8.7 Hz) 3.30 (3 H, s)

1.85 (3 H, s) 1.74 (3 H, s) 1.73 (3 H, s). ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 174.5, 165.6, 149.6, 130.4, 126.4, 118.7, 108.0, 90.2, 55.8, 27.0, 21.1, 20.1, 18.2.

Synthesis of 3-Aryl Oxindole Enol Carbonates



2-Phenoxycarbonyloxy-3-phenyl-indole-1-carboxylic acid phenyl ester (55). To a solution of the known 3-phenyl-1,3-dihydroindol-2-one[27] (0.500 g, 2.39 mmol) in THF (9 mL) was added Et_3N (0.75 mL, 5.38 mmol) at 0 °C. Phenyl chloroformate (0.66 mL, 5.26 mmol) was added to this solution which formed a precipitate and the resulting slurry was stirred at 0 °C for 30 min. The slurry was poured into H_2O and extracted with Et_2O. The combined organic layers were washed with 0.1 M HCl, sat aq $NaHCO_3$, and brine, dried over $MgSO_4$, filtered and concentrated (aspirator). The residue was purified by flash chromatography (silica gel) using 88:12 hexane/Et_2O as the eluent, yielding pure enol carbonate **55** as a slightly yellow crystalline solid (0.935 g, 87%). Analytical tlc, 1:1 Et_2O/hexane, Rf= 0.60. Molecular ion calculated for $C_{28}H_{19}NO_5$: 449.1263; [M^+], EIMS found m/z= 449.1272; IR (neat, cm^{-1}) 1792, C=O; 1755, C=O; 1260, C-O; 500 MHz NMR ($CDCl_3$, ppm) δ 8.25 (1 H, d, J= 8.8 Hz) 7.70 (1 H, d, J= 7.3 Hz) 7.65 (2 H, d, J= 8.3 Hz) 7.53-7.50 (2 H, m) 7.47-7.39 (4 H, m) 7.34-7.27 (6 H, m) 7.20-7.17 (1 H, m) 7.02 (2 H, d, J= 7.8 Hz). ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 151.5, 151.1, 150.2, 148.9, 136.8, 132.6, 130.5, 130.1, 129.8, 129.4, 129.2, 128.3, 127.1, 127.0, 126.8, 125.8, 124.5, 121.8, 121.0, 120.3, 116.0, 112.3.



Carboxyl migration of 55: Enol carbonate **55** (45 mg, 0.100 mmol) and (*R*)-**1** (4.4 mg, 0.010 mmol) were dissolved in *t*-amyl alcohol (2 mL) at rt and were warmed to 40 °C. After stirring for 18 h, the solution was allowed to cool to rt and was quenched with iodomethane (0.1 mL). The solution was then concentrated (N_2 stream), the residue was filtered through a silica plug with Et_2O as the eluent, and concentrated (aspirator) yielding *C*-carboxyl oxindole **56** as a yellow crystalline solid (42 mg, 93%, 86% ee). HPLC (Chiralpak AD, 4.6mm x 25 cm, 90:10 hexane/isopropanol, 1.0 mL/min) T_R = 13.2 min (major), T_R = 18.2 min (minor). Analytical tlc, 4:1 hexane/Et_2O, Rf= 0.30. Molecular ion calculated for $C_{28}H_{19}NO_5$: 449.1263; [M^+], EIMS found m/z= 449.1262; IR (neat, cm^{-1}) 1748, C=O; 1156, C-O; 500 MHz NMR ($CDCl_3$, ppm) δ 8.16-8.14 (1 H, m) 7.65-7.63 (1 H, m) 7.57-7.53 (1 H, m) 7.45-7.37 (14 H, m) 7.04-7.02 (2 H, m). ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 170.1, 167.3, 150.6, 150.3, 149.6, 140.3, 135.1, 130.8, 129.8, 129.7, 129.2, 129.1, 128.5, 126.8, 126.7, 126.1, 125.9, 125.7, 121.7, 121.3, 116.4, 64.9.

Crystallographic Analysis of ***11***

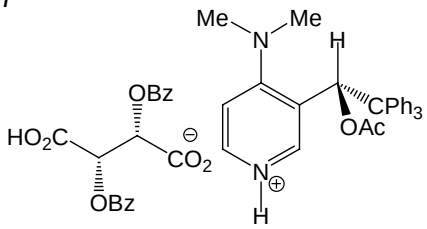
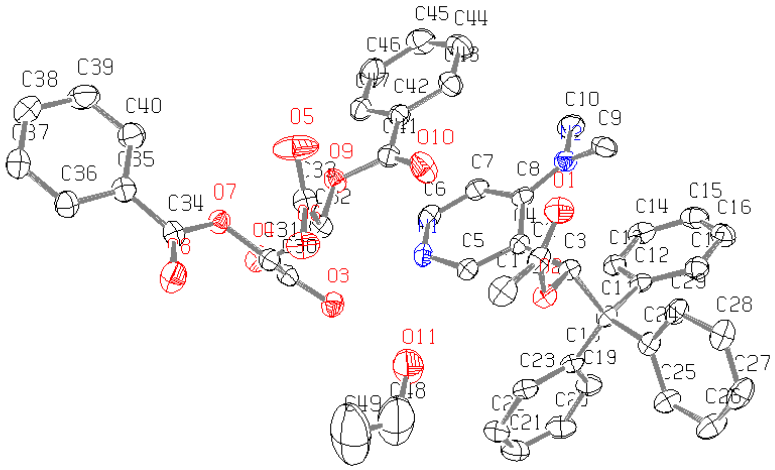
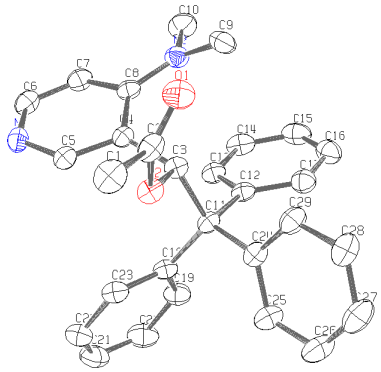


Figure S-1. (+)-**1**•Dibenzoyl-(L)-tartaric acid (**11**)



(a)



(b)

Figure S-2. a) ORTEP of **11** b) Acid and solvent omitted for clarity.

Colorless plates of (+)-**1**•Dibenzoyl-(L)-tartaric acid•EtOH (**11**) were grown from a ethanol/hexanes solution at 22° C. A crystal of dimensions 0.26 x 0.24 x 0.08 mm was mounted on a standard Bruker SMART CCD-based X-ray diffractometer equipped with a LT-2 low temperature device and normal focus Mo-target X-ray tube (λ = 0.71073 Å) operated at 2000 W power (50 kV, 40 mA). The X-ray intensities were measured at 150(2) K; the detector was placed at a distance 4.950 cm from the crystal. A total of 3696 frames were collected with a scan width of 0.2° in ω and phi with an exposure time of 30 s/frame. The integration of the data yielded a total of 24224 reflections to a maximum 2θ value of 56.72° of which 5681 were independent and 4828 were greater than $2\sigma(I)$. The final cell constants (Table 1) were based on the xyz centroids of 4877 reflections above $10\sigma(I)$. Analysis of the data showed negligible decay during data collection; the data were processed with SADABS, no correction for absorption was necessary. The structure was solved and refined with the Bruker SHELXTL (version 5.10) software package, using the space group P2(1) with Z = 2 for the formula $C_{47}H_{42}N_2O_{10}$•(C_2H_5OH). All non-hydrogen atoms were refined anisotropically with the hydrogen atoms placed in idealized positions. Full matrix least-squares refinement based on F^2 converged at R1 = 0.0384 and wR2 = 0.0908 [based on $I > 2\sigma(I)$], R1 = 0.0501 and wR2 = 0.0961 for all data. The relative configuration for the structure was established by assigning the known sites of C31 and C32 and the (*R*)-enantiomer. Additional details are presented in Table B-1.

Sheldrick, G.M. SHELXTL, v. 5.10; Bruker Analytical X-ray, Madison, WI, 1997.

Sheldrick, G.M. SADABS. Program for Empirical Absorption Correction of Area Detector Data, University of Gottingen: Gottingen, Germany, 1996.

Saint Plus, v. 6.29, Bruker Analytical X-ray, Madison, WI, 2001.

Table S-1. Crystal data and structure refinement for **11**.

Identification code	**11**
Empirical formula	$C_{49}H_{48}N_2O_{11}$
Formula weight	840.89
Temperature	150(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P2(1)
Unit cell dimensions	a = 11.999(2) Å α = 90° b = 7.7101(13) Å β = 92.075(3)° c = 23.028(4) Å γ = 90°
Volume	2129.0(6) $Å^3$
Z, Calculated density	2, 1.312 Mg/m^3
Absorption coefficient	0.093 mm^{-1}
F(000)	888
Crystal size	0.25 x 0.24 x 0.08 mm
θ range for data collection	3.10 to 28.36°
Limiting indices	-16<=h<=16, -10<=k<=10, -30<=l<=30
Reflections collected / unique	24224 / 5681 [R(int) = 0.0359]
Completeness to theta = 28.36	99.4 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5681 / 1 / 568
Goodness-of-fit on F^2	1.040

Final R indices [I>2σ(I)]	R1 = 0.0384, wR2 = 0.0908
R indices (all data)	R1 = 0.0501, wR2 = 0.0961
Absolute structure parameter	0.3(8)
Largest diff. peak and hole	0.429 and -0.451 e.A^{-3}

Table S-2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **11**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
N(1)	-239(2)	3238(3)	7340(1)	28(1)
N(2)	3086(2)	3579(3)	7015(1)	29(1)
O(1)	2087(2)	8542(2)	7599(1)	36(1)
O(2)	1412(1)	6787(2)	8284(1)	26(1)
O(3)	-2330(1)	4467(2)	7488(1)	31(1)
O(4)	-3351(1)	3508(2)	6727(1)	33(1)
O(5)	-2131(2)	9889(3)	6126(1)	58(1)
O(6)	-2655(2)	10411(2)	7027(1)	36(1)
O(7)	-3858(1)	6707(2)	6359(1)	27(1)
O(8)	-5024(2)	8599(3)	6767(1)	41(1)
O(9)	-1513(1)	6568(2)	6413(1)	27(1)
O(10)	48(2)	7993(3)	6686(1)	42(1)
C(1)	484(2)	9425(3)	8127(1)	36(1)
C(2)	1418(2)	8265(3)	7961(1)	28(1)
C(3)	2173(2)	5438(3)	8113(1)	22(1)
C(4)	1545(2)	4335(3)	7650(1)	22(1)
C(5)	408(2)	4265(3)	7681(1)	25(1)
C(6)	220(2)	2150(3)	6960(1)	31(1)
C(7)	1331(2)	2173(3)	6886(1)	29(1)
C(8)	2033(2)	3391(3)	7185(1)	25(1)
C(9)	3733(2)	5165(4)	7085(1)	39(1)
C(10)	3600(2)	2264(4)	6652(1)	42(1)
C(11)	2620(2)	4489(3)	8686(1)	23(1)
C(12)	3623(2)	3381(3)	8491(1)	24(1)
C(13)	3437(2)	1829(3)	8187(1)	27(1)
C(14)	4311(2)	890(3)	7964(1)	34(1)
C(15)	5397(2)	1469(4)	8046(1)	39(1)
C(16)	5603(2)	2973(4)	8360(1)	36(1)
C(17)	4728(2)	3912(3)	8583(1)	32(1)
C(18)	1744(2)	3368(3)	8981(1)	26(1)
C(19)	2046(2)	1809(3)	9251(1)	33(1)
C(20)	1280(2)	824(4)	9546(1)	41(1)
C(21)	190(2)	1366(4)	9579(1)	40(1)
C(22)	-120(2)	2930(4)	9323(1)	36(1)
C(23)	647(2)	3933(3)	9040(1)	29(1)
C(24)	3050(2)	5898(3)	9118(1)	26(1)
C(25)	2993(2)	5636(4)	9716(1)	34(1)
C(26)	3482(2)	6811(4)	10109(1)	44(1)
C(27)	4038(2)	8249(4)	9917(1)	42(1)

C(28)	4092(2)	8543(3)	9326(1)	35(1)
C(29)	3593(2)	7390(3)	8936(1)	30(1)
C(30)	-2957(2)	4670(3)	7042(1)	25(1)
C(31)	-3212(2)	6596(3)	6895(1)	25(1)
C(32)	-2116(2)	7566(3)	6822(1)	25(1)
C(33)	-2300(2)	9429(3)	6609(1)	29(1)
C(34)	-4734(2)	7808(3)	6348(1)	26(1)
C(35)	-5311(2)	7878(3)	5769(1)	28(1)
C(36)	-6373(2)	8602(3)	5730(1)	31(1)
C(37)	-6941(2)	8707(4)	5198(1)	36(1)
C(38)	-6456(2)	8082(4)	4704(1)	40(1)
C(39)	-5412(3)	7345(4)	4742(1)	46(1)
C(40)	-4827(2)	7252(4)	5271(1)	39(1)
C(41)	-408(2)	6875(3)	6402(1)	27(1)
C(42)	145(2)	5655(3)	6006(1)	27(1)
C(43)	1282(2)	5874(3)	5918(1)	33(1)
C(44)	1824(2)	4784(4)	5543(1)	40(1)
C(45)	1248(2)	3453(4)	5264(1)	43(1)
C(46)	124(2)	3197(4)	5361(1)	43(1)
C(47)	-424(2)	4295(4)	5731(1)	32(1)
O(11)	-1474(2)	6381(4)	8393(1)	62(1)
C(48)	-2082(4)	6955(12)	8845(2)	144(3)
C(49)	-2987(5)	7765(11)	8799(3)	148(3)

Table S-3. Bond lengths [Å] and angles [°] for **11**.

N(1)-C(5)	1.342(3)
N(1)-C(6)	1.344(3)
N(2)-C(8)	1.344(3)
N(2)-C(9)	1.454(3)
N(2)-C(10)	1.465(3)
O(1)-C(2)	1.196(3)
O(2)-C(2)	1.361(3)
O(2)-C(3)	1.448(3)
O(3)-C(30)	1.260(3)
O(4)-C(30)	1.236(3)
O(5)-C(33)	1.192(3)
O(6)-C(33)	1.309(3)
O(7)-C(34)	1.350(3)
O(7)-C(31)	1.435(3)
O(8)-C(34)	1.203(3)

O(9)-C(41)	1.347(3)
O(9)-C(32)	1.432(3)
O(10)-C(41)	1.202(3)
C(1)-C(2)	1.495(3)
C(3)-C(4)	1.539(3)
C(3)-C(11)	1.584(3)
C(4)-C(5)	1.370(3)
C(4)-C(8)	1.438(3)
C(6)-C(7)	1.350(3)
C(7)-C(8)	1.423(3)
C(11)-C(18)	1.539(3)
C(11)-C(24)	1.548(3)
C(11)-C(12)	1.556(3)
C(12)-C(17)	1.396(3)
C(12)-C(13)	1.399(3)
C(13)-C(14)	1.389(3)
C(14)-C(15)	1.383(4)
C(15)-C(16)	1.384(4)
C(16)-C(17)	1.388(4)
C(18)-C(19)	1.395(3)
C(18)-C(23)	1.397(3)
C(19)-C(20)	1.389(4)
C(20)-C(21)	1.377(4)
C(21)-C(22)	1.388(4)
C(22)-C(23)	1.383(3)
C(24)-C(29)	1.394(3)
C(24)-C(25)	1.398(3)
C(25)-C(26)	1.395(4)
C(26)-C(27)	1.375(4)
C(27)-C(28)	1.384(4)
C(28)-C(29)	1.386(3)
C(30)-C(31)	1.551(3)
C(31)-C(32)	1.527(3)
C(32)-C(33)	1.532(3)
C(34)-C(35)	1.483(3)
C(35)-C(40)	1.390(3)
C(35)-C(36)	1.391(3)
C(36)-C(37)	1.383(3)
C(37)-C(38)	1.384(4)
C(38)-C(39)	1.375(4)
C(39)-C(40)	1.387(3)
C(41)-C(42)	1.484(3)
C(42)-C(47)	1.392(3)
C(42)-C(43)	1.396(3)
C(43)-C(44)	1.384(4)
C(44)-C(45)	1.383(4)
C(45)-C(46)	1.390(4)

C(46)-C(47)	1.383(4)
O(11)-C(48)	1.366(5)
C(48)-C(49)	1.253(7)

C(5)-N(1)-C(6)	120.4(2)
C(8)-N(2)-C(9)	124.2(2)
C(8)-N(2)-C(10)	120.7(2)
C(9)-N(2)-C(10)	114.3(2)
C(2)-O(2)-C(3)	115.90(17)
C(34)-O(7)-C(31)	116.71(17)
C(41)-O(9)-C(32)	116.04(17)
O(1)-C(2)-O(2)	123.2(2)
O(1)-C(2)-C(1)	126.8(2)
O(2)-C(2)-C(1)	110.0(2)
O(2)-C(3)-C(4)	106.68(16)
O(2)-C(3)-C(11)	107.66(16)
C(4)-C(3)-C(11)	117.64(17)
C(5)-C(4)-C(8)	116.84(19)
C(5)-C(4)-C(3)	116.77(19)
C(8)-C(4)-C(3)	126.39(19)
N(1)-C(5)-C(4)	123.3(2)
N(1)-C(6)-C(7)	120.2(2)
C(6)-C(7)-C(8)	121.2(2)
N(2)-C(8)-C(7)	118.5(2)
N(2)-C(8)-C(4)	125.1(2)
C(7)-C(8)-C(4)	116.37(19)
C(18)-C(11)-C(24)	109.08(17)
C(18)-C(11)-C(12)	111.56(18)
C(24)-C(11)-C(12)	109.13(17)
C(18)-C(11)-C(3)	114.28(17)
C(24)-C(11)-C(3)	107.77(17)
C(12)-C(11)-C(3)	104.81(16)
C(17)-C(12)-C(13)	117.4(2)
C(17)-C(12)-C(11)	122.4(2)
C(13)-C(12)-C(11)	120.15(19)
C(14)-C(13)-C(12)	121.4(2)
C(15)-C(14)-C(13)	120.1(2)
C(14)-C(15)-C(16)	119.4(2)
C(15)-C(16)-C(17)	120.4(2)
C(16)-C(17)-C(12)	121.2(2)
C(19)-C(18)-C(23)	117.1(2)
C(19)-C(18)-C(11)	120.7(2)
C(23)-C(18)-C(11)	121.9(2)
C(20)-C(19)-C(18)	121.5(2)
C(21)-C(20)-C(19)	120.5(2)
C(20)-C(21)-C(22)	118.7(2)
C(23)-C(22)-C(21)	120.9(2)

C(22)-C(23)-C(18)	121.1(2)
C(29)-C(24)-C(25)	117.1(2)
C(29)-C(24)-C(11)	122.29(19)
C(25)-C(24)-C(11)	120.3(2)
C(26)-C(25)-C(24)	120.8(2)
C(27)-C(26)-C(25)	120.9(2)
C(26)-C(27)-C(28)	119.3(2)
C(27)-C(28)-C(29)	119.9(3)
C(28)-C(29)-C(24)	122.0(2)
O(4)-C(30)-O(3)	126.3(2)
O(4)-C(30)-C(31)	119.80(19)
O(3)-C(30)-C(31)	113.86(19)
O(7)-C(31)-C(32)	108.50(17)
O(7)-C(31)-C(30)	109.98(18)
C(32)-C(31)-C(30)	109.20(17)
O(9)-C(32)-C(31)	105.47(17)
O(9)-C(32)-C(33)	111.30(18)
C(31)-C(32)-C(33)	112.36(18)
O(5)-C(33)-O(6)	125.9(2)
O(5)-C(33)-C(32)	123.5(2)
O(6)-C(33)-C(32)	110.68(19)
O(8)-C(34)-O(7)	123.5(2)
O(8)-C(34)-C(35)	124.3(2)
O(7)-C(34)-C(35)	112.17(19)
C(40)-C(35)-C(36)	119.8(2)
C(40)-C(35)-C(34)	122.3(2)
C(36)-C(35)-C(34)	118.0(2)
C(37)-C(36)-C(35)	120.0(2)
C(36)-C(37)-C(38)	120.0(2)
C(39)-C(38)-C(37)	120.0(2)
C(38)-C(39)-C(40)	120.6(2)
C(39)-C(40)-C(35)	119.5(2)
O(10)-C(41)-O(9)	123.1(2)
O(10)-C(41)-C(42)	125.7(2)
O(9)-C(41)-C(42)	111.26(19)
C(47)-C(42)-C(43)	119.4(2)
C(47)-C(42)-C(41)	122.3(2)
C(43)-C(42)-C(41)	118.3(2)
C(44)-C(43)-C(42)	120.0(2)
C(45)-C(44)-C(43)	120.2(2)
C(44)-C(45)-C(46)	120.1(2)
C(47)-C(46)-C(45)	119.9(3)
C(46)-C(47)-C(42)	120.3(2)
C(49)-C(48)-O(11)	125.7(6)

Symmetry transformations used to generate equivalent atoms:

Table S-4. Anisotropic displacement parameters (A^2 x 10^3) for **11**.
The anisotropic displacement factor exponent takes the form:
$-2\pi^2$ [h^2 a^{*2} U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
N(1)	24(1)	28(1)	32(1)	2(1)	-4(1)	-2(1)
N(2)	30(1)	32(1)	25(1)	-1(1)	4(1)	4(1)
O(1)	44(1)	26(1)	38(1)	7(1)	3(1)	0(1)
O(2)	32(1)	18(1)	27(1)	-1(1)	0(1)	4(1)
O(3)	30(1)	28(1)	34(1)	4(1)	-3(1)	2(1)
O(4)	42(1)	22(1)	36(1)	-1(1)	-2(1)	1(1)
O(5)	98(2)	38(1)	39(1)	12(1)	24(1)	24(1)
O(6)	52(1)	20(1)	37(1)	-1(1)	7(1)	4(1)
O(7)	26(1)	26(1)	29(1)	-1(1)	-1(1)	4(1)
O(8)	40(1)	42(1)	41(1)	-16(1)	-6(1)	17(1)
O(9)	24(1)	26(1)	31(1)	-5(1)	4(1)	-1(1)
O(10)	35(1)	39(1)	54(1)	-18(1)	7(1)	-10(1)
C(1)	44(1)	22(1)	41(1)	-1(1)	-3(1)	8(1)
C(2)	36(1)	20(1)	29(1)	-2(1)	-8(1)	0(1)
C(3)	28(1)	17(1)	22(1)	-1(1)	1(1)	3(1)
C(4)	26(1)	18(1)	22(1)	2(1)	-2(1)	0(1)
C(5)	28(1)	21(1)	25(1)	1(1)	-1(1)	2(1)
C(6)	40(1)	23(1)	29(1)	0(1)	-7(1)	-5(1)
C(7)	38(1)	26(1)	25(1)	-4(1)	0(1)	2(1)
C(8)	31(1)	22(1)	21(1)	4(1)	-1(1)	4(1)
C(9)	37(1)	49(2)	31(1)	0(1)	11(1)	-12(1)
C(10)	40(1)	52(2)	32(1)	-8(1)	6(1)	17(1)
C(11)	28(1)	21(1)	21(1)	-1(1)	-2(1)	1(1)
C(12)	31(1)	21(1)	20(1)	3(1)	0(1)	6(1)
C(13)	33(1)	24(1)	25(1)	2(1)	0(1)	4(1)
C(14)	48(2)	27(1)	28(1)	1(1)	4(1)	9(1)
C(15)	43(1)	41(1)	33(1)	6(1)	10(1)	16(1)
C(16)	30(1)	42(1)	38(1)	9(1)	5(1)	6(1)
C(17)	33(1)	32(1)	30(1)	2(1)	1(1)	2(1)
C(18)	33(1)	26(1)	20(1)	-2(1)	2(1)	1(1)
C(19)	40(1)	30(1)	29(1)	4(1)	5(1)	4(1)

C(20)	56(2)	32(1)	35(1)	11(1)	9(1)	0(1)
C(21)	47(2)	42(2)	33(1)	5(1)	11(1)	-7(1)
C(22)	35(1)	43(1)	30(1)	-2(1)	8(1)	0(1)
C(23)	36(1)	28(1)	23(1)	0(1)	3(1)	4(1)
C(24)	29(1)	24(1)	26(1)	-4(1)	-3(1)	5(1)
C(25)	44(1)	34(1)	25(1)	-2(1)	-1(1)	1(1)
C(26)	60(2)	46(2)	26(1)	-7(1)	-5(1)	-2(1)
C(27)	53(2)	36(1)	38(1)	-13(1)	-13(1)	3(1)
C(28)	38(1)	26(1)	40(1)	-4(1)	-10(1)	4(1)
C(29)	36(1)	26(1)	28(1)	0(1)	-6(1)	3(1)
C(30)	22(1)	23(1)	30(1)	2(1)	5(1)	1(1)
C(31)	25(1)	23(1)	26(1)	2(1)	1(1)	2(1)
C(32)	26(1)	21(1)	27(1)	-2(1)	3(1)	2(1)
C(33)	29(1)	23(1)	34(1)	1(1)	1(1)	-1(1)
C(34)	22(1)	21(1)	36(1)	0(1)	1(1)	-1(1)
C(35)	29(1)	22(1)	33(1)	3(1)	1(1)	0(1)
C(36)	28(1)	30(1)	35(1)	-5(1)	-1(1)	0(1)
C(37)	30(1)	35(1)	42(1)	1(1)	-5(1)	2(1)
C(38)	45(2)	43(2)	32(1)	4(1)	-6(1)	1(1)
C(39)	56(2)	51(2)	30(1)	1(1)	9(1)	12(2)
C(40)	39(1)	43(1)	37(1)	2(1)	5(1)	12(1)
C(41)	28(1)	26(1)	28(1)	2(1)	0(1)	-2(1)
C(42)	27(1)	27(1)	26(1)	4(1)	0(1)	3(1)
C(43)	28(1)	30(1)	39(1)	5(1)	4(1)	0(1)
C(44)	33(1)	43(2)	46(2)	9(1)	11(1)	7(1)
C(45)	47(2)	44(2)	39(1)	-5(1)	8(1)	14(1)
C(46)	44(2)	48(2)	38(1)	-16(1)	-5(1)	4(1)
C(47)	29(1)	40(1)	28(1)	-4(1)	-1(1)	1(1)
O(11)	48(1)	77(2)	62(1)	-33(1)	2(1)	8(1)
C(48)	77(3)	243(9)	110(4)	-111(5)	-13(3)	36(4)
C(49)	81(3)	175(7)	187(7)	-101(6)	-17(4)	45(4)

Table S-5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for **11**.

	x	y	z	U(eq)
H(1A)	-969	3277	7365	33
H(6)	-2840(30)	11580(60)	6927(15)	64(10)
H(1B)	730	10636	8114	54
H(1C)	264	9141	8521	54
H(1D)	-154	9259	7855	54
H(3A)	2821	6001	7927	27

H(5A)	59	4980	7957	30
H(1a)	-239	1361	6743	37
H(7A)	1649	1361	6630	35
H(1a)	3227	6159	7105	58
H(9B)	4215	5305	6754	58
H(9C)	4194	5100	7445	58
H(10A)	3386	1106	6783	62
H(10B)	4414	2381	6683	62
H(10C)	3345	2425	6246	62
H(13A)	2696	1410	8133	33
H(14A)	4164	-153	7755	41
H(15A)	5996	840	7888	47
H(11a)	6348	3366	8424	44
H(17A)	4884	4934	8801	38
H(11a)	2793	1412	9232	39
H(20A)	1509	-232	9726	49
H(21A)	-338	682	9774	49
H(22A)	-869	3317	9342	43
H(23A)	424	5023	8883	35
H(25A)	2618	4645	9857	41
H(21a)	3431	6616	10515	53
H(27A)	4380	9032	10188	51
H(28A)	4471	9535	9189	42
H(21a)	3623	7622	8531	36
H(31A)	-3633	7135	7215	30
H(32A)	-1688	7587	7203	30
H(31a)	-6708	9025	6070	37
H(37A)	-7664	9209	5172	43
H(38A)	-6845	8162	4338	49
H(31a)	-5089	6895	4402	55
H(40A)	-4100	6763	5294	47
H(43A)	1683	6770	6116	39
H(44A)	2593	4951	5477	48
H(45A)	1621	2713	5004	52
H(41a)	-268	2269	5175	52
H(47A)	-1193	4120	5797	39
H(11)	-1895	5855	8153	94
H(48A)	-2233	5918	9083	173
H(48B)	-1572	7697	9084	173
H(41a)	-2861	8898	8620	222
H(49B)	-3285	7931	9186	222
H(49C)	-3521	7100	8557	222

Table S-6. Hydrogen bonds for **11** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1A)...O(3)	0.88	1.90	2.714(2)	152.6
O(11)-H(11)...O(3)	0.84	1.92	2.725(3)	158.8
O(6)-H(6)...O(4)#1	0.95(4)	1.67(4)	2.614(2)	171(3)

Symmetry transformations used to generate equivalent atoms: #1 x,y+1,z

Crystallographic Analysis of ***45e***

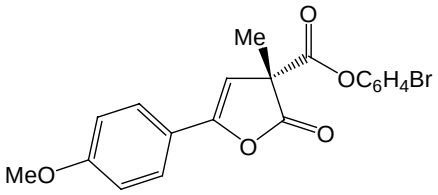


Figure S-3. Furanone **45e**

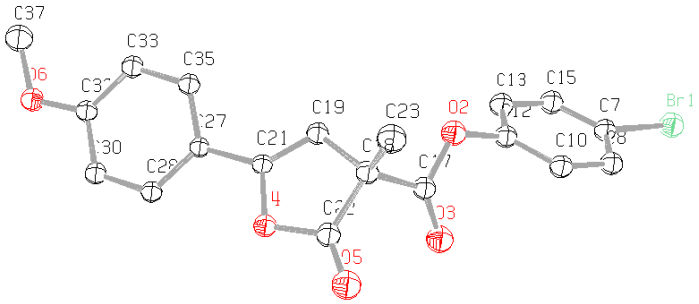


Figure S-4. ORTEP of **45e**

Colorless needles of **45e** were grown from an ethyl acetate/hexanes solution at 22 ºC. A crystal of dimensions 0.36 x 0.34 x 0.20 mm was mounted on a standard Bruker SMART CCD-based X-ray diffractometer equipped with a LT-2 low temperature device and normal focus Mo-target X-ray tube (λ = 0.71073 Å) operated at 2000 W power (50 kV, 40 mA). The X-ray intensities were measured at 123(2) K; the detector was placed at a distance 4.980 cm from the crystal. A total of 3227 frames were collected with a scan width of 0.2° in ω and phi with an exposure time of 15 s/frame. The integration of the data yielded a total of 17808 reflections to a maximum 2θ value of 56.66° of which 4261 were independent and 4071 were greater than $2\sigma(I)$. The final cell constants (Table 1) were based on the xyz centroids of 5220 reflections above $10\sigma(I)$. Analysis of the data showed negligible decay during data collection; the data were processed with SADABS and corrected for absorption. The structure was solved and refined with the Bruker SHELXTL (version 5.10) software package, using the space group P2(1)2(1)2(1) with Z = 4 for the formula $C_{19}H_{15}O_5Br$. All non-hydrogen atoms were refined anisotropically with the hydrogen atoms placed in idealized positions. Full matrix least-squares refinement based on F^2 converged at R1 = 0.0220 and wR2 = 0.0560 [based on $I > 2\sigma(I)$], R1 = 0.0238 and wR2 = 0.0571 for all data. Additional details are presented in Table 1 and are given as Supporting Information in a CIF file.

Sheldrick, G.M. SHELXTL, v. 6.12; Bruker Analytical X-ray, Madison, WI, 2001.

Sheldrick, G.M. SADABS, v. 2.10. Program for Empirical Absorption Correction of Area Detector Data, University of Gottingen: Gottingen, Germany, 2003.

Saint Plus, v. 7.01, Bruker Analytical X-ray, Madison, WI, 2003.

Table S-7. Crystal data and structure refinement for **45e**.

Identification code	**45e**
Empirical formula	$C_{19}H_{15}BrO_5$
Formula weight	403.22
Temperature	123(2) K
Wavelength	0.71073 Å
Crystal system, space group	Orthorhombic, P2(1)2(1)2(1)
Unit cell dimensions	a = 6.5133(13) Å α = 90° b = 13.746(3) Å β = 90° c = 19.125(4) Å γ = 90°
Volume	1712.3(6) $Å^3$
Z, Calculated density	4, 1.564 Mg/m^3
Absorption coefficient	2.427 mm^{-1}
F(000)	816
Crystal size	0.36 x 0.34 x 0.20 mm
θ range for data collection	2.96 to 28.3°
Limiting indices	-8<=h<=8, -18<=k<=18, -25<=l<=25
Reflections collected / unique	17808 / 4261 [R(int) = 0.0280]
Completeness to theta = 28.33	99.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.6424 and 0.4753
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4261 / 0 / 228

Goodness-of-fit on F^2	1.034
Final R indices [I>2sigma(I)]	R1 = 0.0220, wR2 = 0.0560
R indices (all data)	R1 = 0.0238, wR2 = 0.0571
Absolute structure parameter	-0.004(5)
Largest diff. peak and hole	0.428 and -0.457 $e.A^{-3}$

Table S-8. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **45e**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Br(1)	2358(1)	8293(1)	-735(1)	32(1)
O(1)	5679(2)	9571(1)	2058(1)	28(1)
O(2)	8513(2)	8630(1)	2068(1)	32(1)
O(3)	9324(2)	9060(1)	4030(1)	22(1)
O(4)	11518(2)	9373(1)	3154(1)	35(1)
O(5)	4025(2)	7945(1)	6708(1)	26(1)
C(1)	3453(3)	8646(1)	149(1)	24(1)
C(2)	5386(3)	9068(1)	174(1)	24(1)
C(3)	6179(2)	9362(1)	813(1)	24(1)
C(4)	5029(3)	9205(1)	1410(1)	23(1)
C(5)	3120(3)	8767(1)	1391(1)	27(1)
C(6)	2316(2)	8483(1)	748(1)	27(1)
C(7)	7474(3)	9238(1)	2329(1)	22(1)
C(8)	7854(2)	9762(1)	3018(1)	23(1)
C(9)	6260(2)	9518(1)	3557(1)	21(1)
C(10)	7173(2)	9147(1)	4113(1)	18(1)
C(11)	9802(2)	9376(1)	3369(1)	24(1)
C(12)	8071(3)	10867(1)	2893(1)	34(1)
C(13)	6380(2)	8846(1)	4796(1)	18(1)
C(14)	7524(2)	8272(1)	5260(1)	20(1)
C(15)	6689(2)	7988(1)	5892(1)	22(1)
C(16)	4709(2)	8282(1)	6080(1)	21(1)
C(17)	3571(2)	8865(1)	5629(1)	23(1)
C(18)	4403(2)	9136(1)	4988(1)	21(1)
C(19)	2090(3)	8284(2)	6948(1)	36(1)

Table S-9. Bond lengths [Å] and angles [°] for **45e**.

Br(1)-C(1)	1.8988(16)
O(1)-C(7)	1.359(2)
O(1)-C(4)	1.403(2)
O(2)-C(7)	1.185(2)
O(3)-C(11)	1.373(2)

O(3)-C(10)	1.4150(17)
O(4)-C(11)	1.191(2)
O(5)-C(16)	1.3635(19)
O(5)-C(19)	1.420(2)
C(1)-C(6)	1.382(2)
C(1)-C(2)	1.387(2)
C(2)-C(3)	1.387(2)
C(3)-C(4)	1.382(2)
C(4)-C(5)	1.382(2)
C(5)-C(6)	1.393(2)
C(7)-C(8)	1.523(2)
C(8)-C(9)	1.501(2)
C(8)-C(11)	1.530(2)
C(8)-C(12)	1.543(2)
C(9)-C(10)	1.321(2)
C(10)-C(13)	1.464(2)
C(13)-C(18)	1.397(2)
C(13)-C(14)	1.401(2)
C(14)-C(15)	1.383(2)
C(15)-C(16)	1.398(2)
C(16)-C(17)	1.390(2)
C(17)-C(18)	1.391(2)

C(7)-O(1)-C(4)	118.39(13)
C(11)-O(3)-C(10)	107.58(12)
C(16)-O(5)-C(19)	117.61(13)
C(6)-C(1)-C(2)	121.73(15)
C(6)-C(1)-Br(1)	119.68(13)
C(2)-C(1)-Br(1)	118.59(13)
C(1)-C(2)-C(3)	119.35(15)
C(4)-C(3)-C(2)	118.72(15)
C(3)-C(4)-C(5)	122.25(16)
C(3)-C(4)-O(1)	120.67(15)
C(5)-C(4)-O(1)	116.82(15)
C(4)-C(5)-C(6)	118.93(16)
C(1)-C(6)-C(5)	119.00(15)
O(2)-C(7)-O(1)	124.62(14)
O(2)-C(7)-C(8)	127.29(15)
O(1)-C(7)-C(8)	108.08(13)
C(9)-C(8)-C(7)	112.06(13)
C(9)-C(8)-C(11)	101.27(13)
C(7)-C(8)-C(11)	110.47(14)
C(9)-C(8)-C(12)	112.94(14)
C(7)-C(8)-C(12)	110.29(13)
C(11)-C(8)-C(12)	109.47(13)
C(10)-C(9)-C(8)	109.14(13)
C(9)-C(10)-O(3)	112.78(13)

C(9)-C(10)-C(13)	131.94(14)
O(3)-C(10)-C(13)	115.24(13)
O(4)-C(11)-O(3)	121.97(15)
O(4)-C(11)-C(8)	128.95(16)
O(3)-C(11)-C(8)	108.97(13)
C(18)-C(13)-C(14)	118.98(14)
C(18)-C(13)-C(10)	118.65(14)
C(14)-C(13)-C(10)	122.38(13)
C(15)-C(14)-C(13)	120.22(14)
C(14)-C(15)-C(16)	120.36(14)
O(5)-C(16)-C(17)	124.59(14)
O(5)-C(16)-C(15)	115.43(14)
C(17)-C(16)-C(15)	119.97(14)
C(16)-C(17)-C(18)	119.51(14)
C(17)-C(18)-C(13)	120.95(15)

Symmetry transformations used to generate equivalent atoms:

Table S-10. Anisotropic displacement parameters (A^2 x 10^3) for **45e**. The anisotropic displacement factor exponent takes the form:

$-2\pi^2 [h^2 a^{*2} U11 + ... + 2 h k a^* b^* U12]$

	U11	U22	U33	U23	U13	U12
Br(1)	41(1)	30(1)	24(1)	-2(1)	-10(1)	-4(1)
O(1)	21(1)	42(1)	22(1)	-7(1)	-6(1)	8(1)
O(2)	27(1)	45(1)	24(1)	-2(1)	-3(1)	13(1)
O(3)	14(1)	32(1)	19(1)	1(1)	-1(1)	1(1)
O(4)	16(1)	61(1)	28(1)	3(1)	0(1)	-3(1)
O(5)	25(1)	32(1)	19(1)	2(1)	4(1)	2(1)
C(1)	30(1)	20(1)	20(1)	0(1)	-6(1)	1(1)
C(2)	29(1)	22(1)	21(1)	4(1)	-1(1)	-1(1)
C(3)	22(1)	25(1)	24(1)	2(1)	-1(1)	-2(1)
C(4)	20(1)	28(1)	20(1)	-1(1)	-3(1)	5(1)
C(5)	21(1)	36(1)	22(1)	2(1)	1(1)	1(1)
C(6)	22(1)	29(1)	29(1)	1(1)	-3(1)	-2(1)
C(7)	17(1)	31(1)	19(1)	4(1)	1(1)	-2(1)
C(8)	17(1)	31(1)	20(1)	2(1)	0(1)	-1(1)
C(9)	17(1)	28(1)	19(1)	-3(1)	0(1)	2(1)
C(10)	14(1)	20(1)	20(1)	-3(1)	1(1)	0(1)
C(11)	18(1)	35(1)	20(1)	0(1)	-2(1)	-3(1)
C(12)	39(1)	32(1)	32(1)	6(1)	-9(1)	-7(1)
C(13)	18(1)	18(1)	17(1)	-3(1)	-1(1)	-1(1)
C(14)	17(1)	22(1)	21(1)	-3(1)	-2(1)	1(1)
C(15)	21(1)	23(1)	20(1)	-1(1)	-2(1)	1(1)
C(16)	22(1)	25(1)	18(1)	-4(1)	1(1)	-3(1)
C(17)	20(1)	26(1)	22(1)	-3(1)	2(1)	3(1)
C(18)	20(1)	22(1)	21(1)	-3(1)	-2(1)	3(1)
C(19)	28(1)	49(1)	29(1)	6(1)	9(1)	8(1)

Table S-11. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for **45e**.

	x	y	z	U(eq)
H(2A)	6160	9155	-242	29
H(3A)	7488	9665	840	29
H(5A)	2368	8661	1810	32
H(1a)	1005	8182	721	32
H(1a)	4824	9614	3506	26
H(12A)	6772	11126	2714	51
H(12B)	9165	10985	2552	51
H(12C)	8413	11190	3335	51
H(14A)	8879	8078	5139	24
H(15A)	7463	7589	6200	26
H(17A)	2235	9076	5758	27
H(18A)	3616	9525	4677	25
H(11a)	2116	8995	6982	53
H(19B)	1799	8005	7409	53
H(19C)	1018	8085	6618	53

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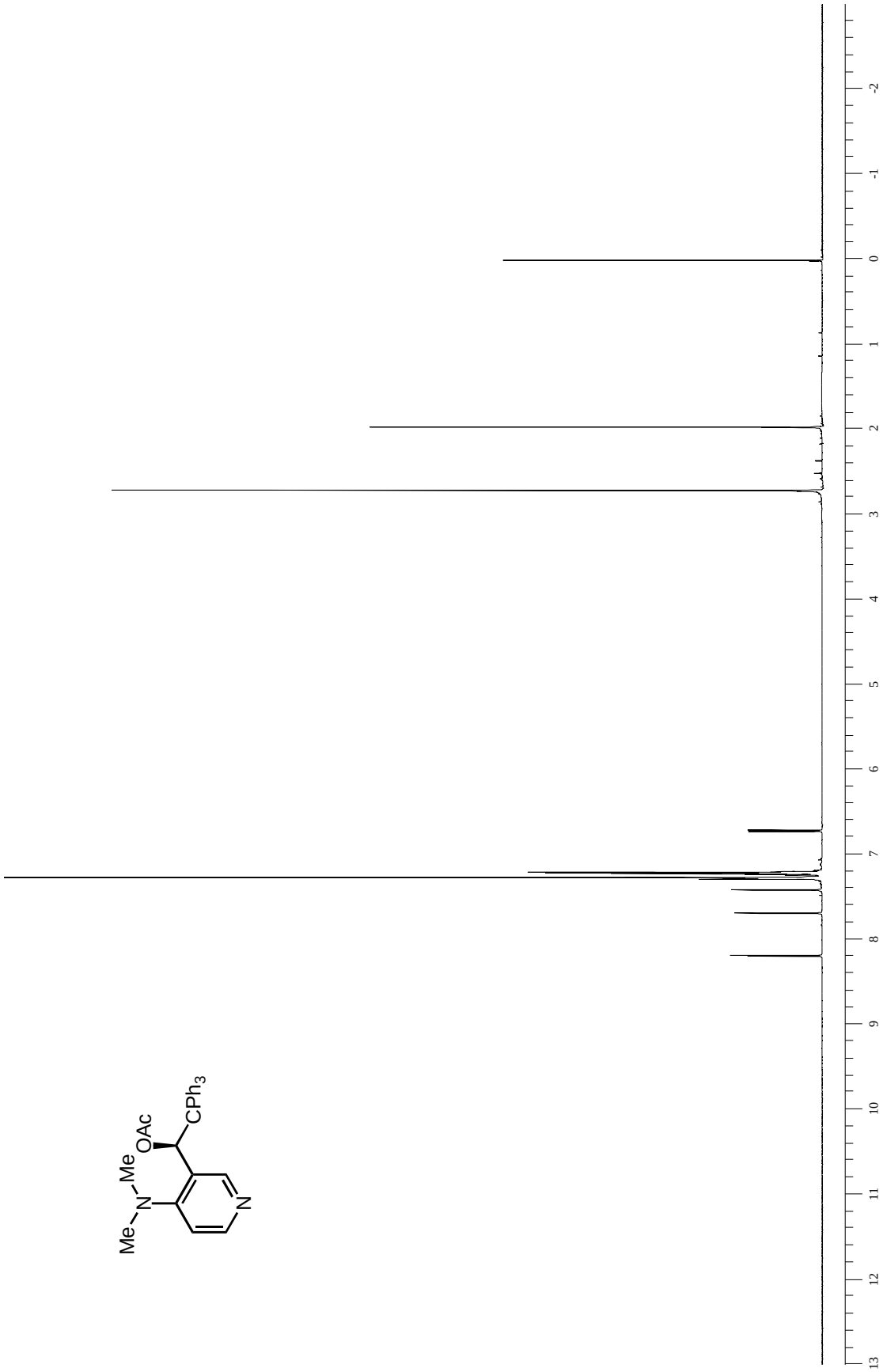
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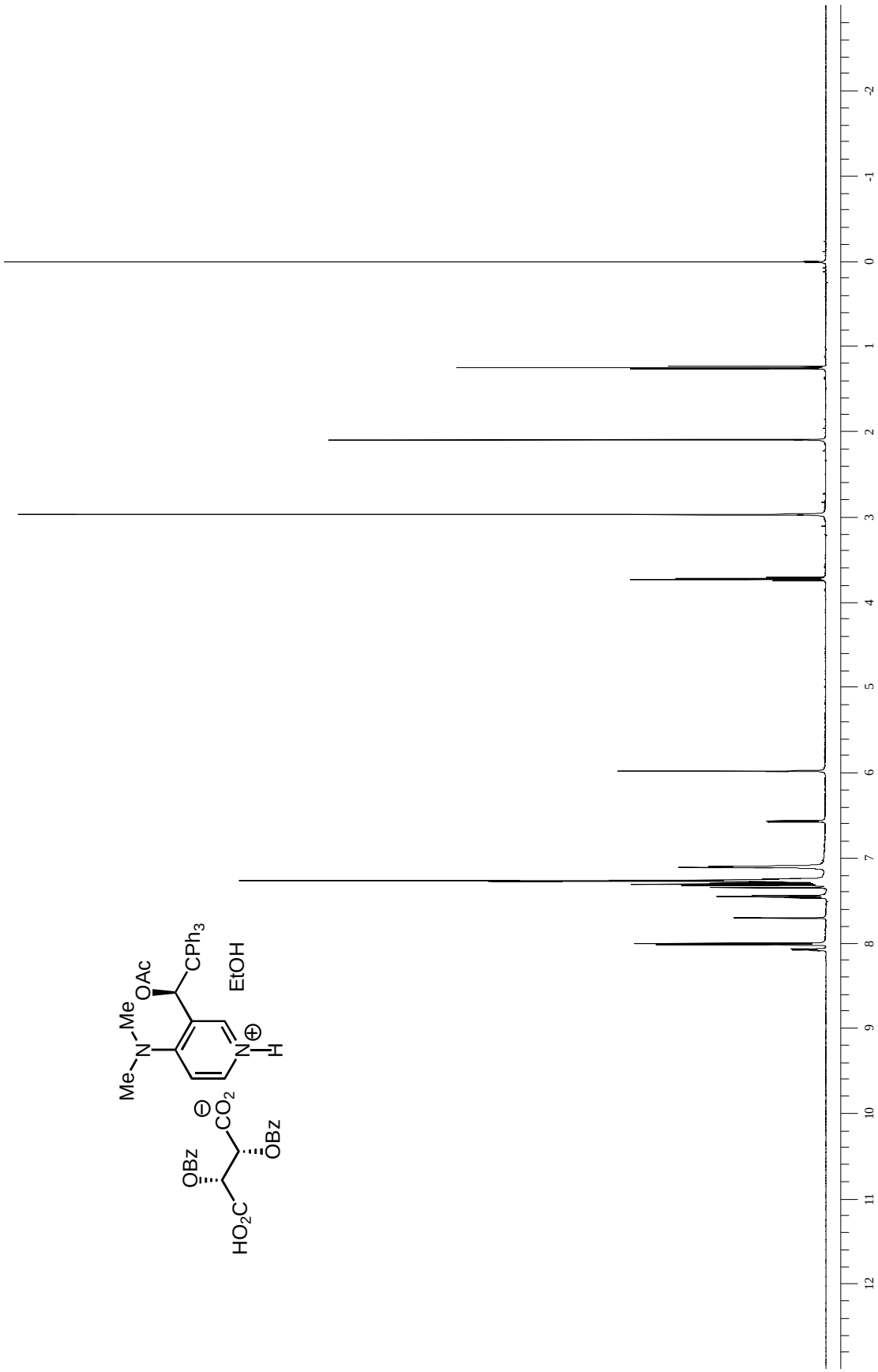
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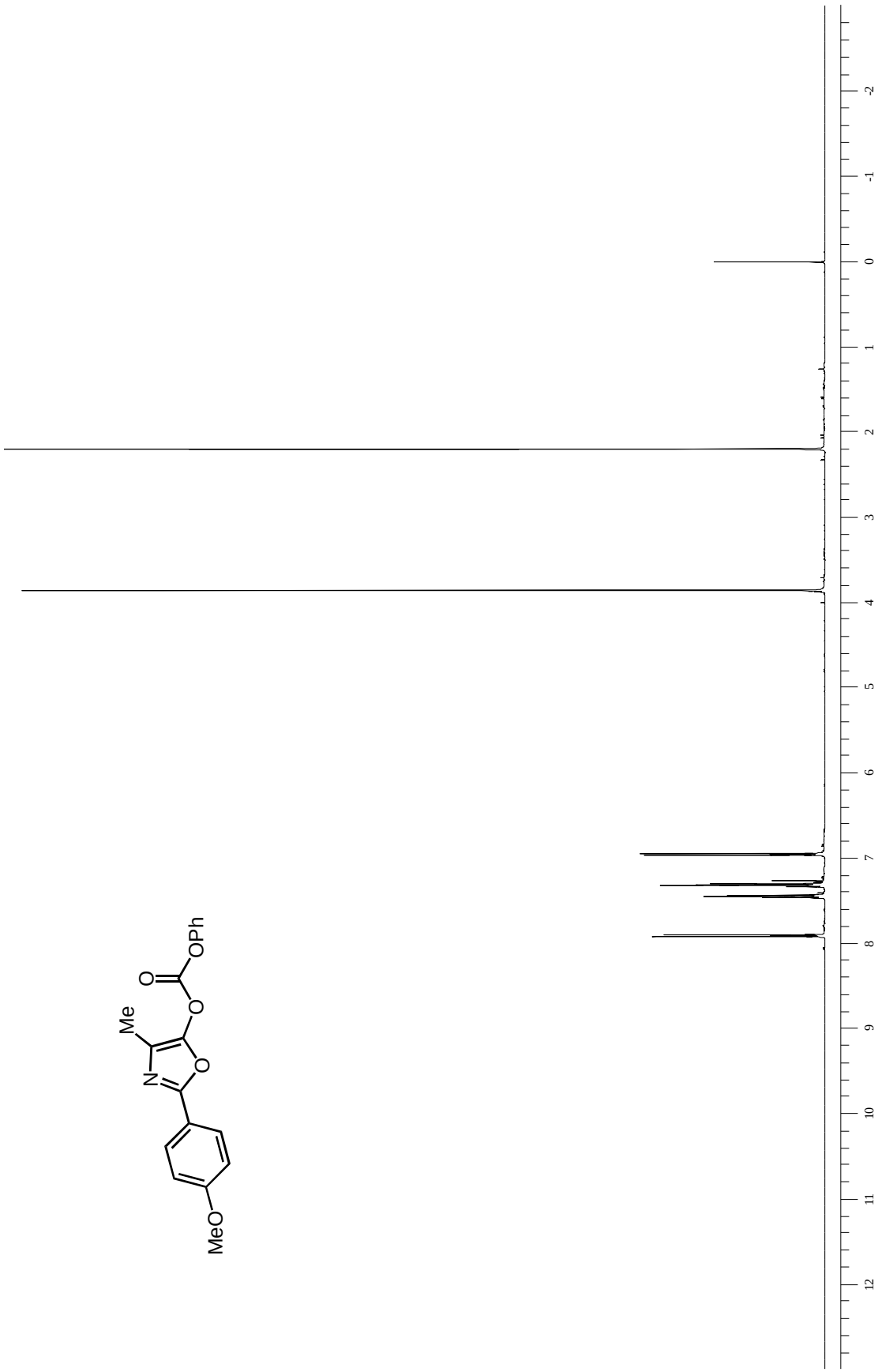
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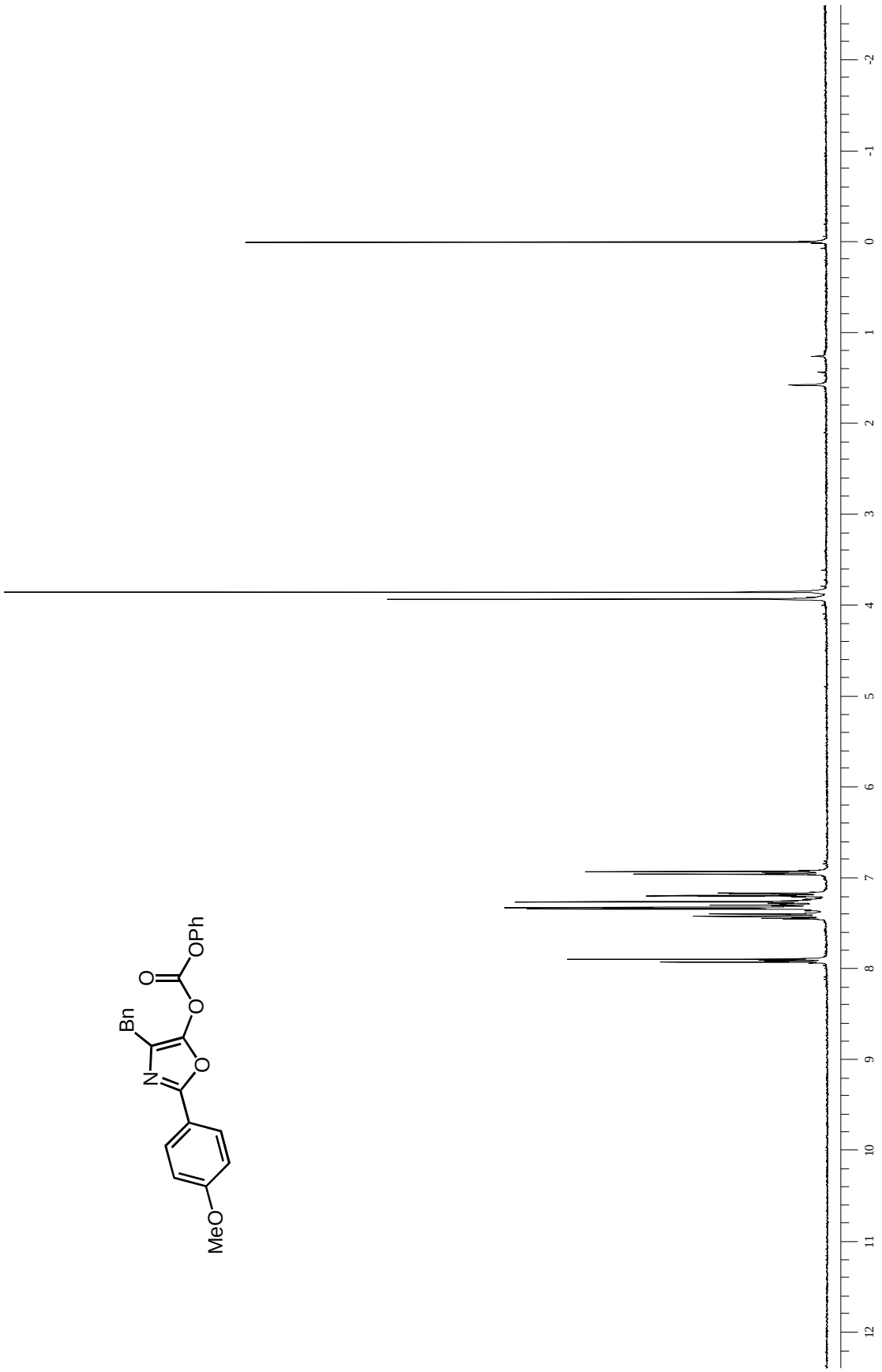
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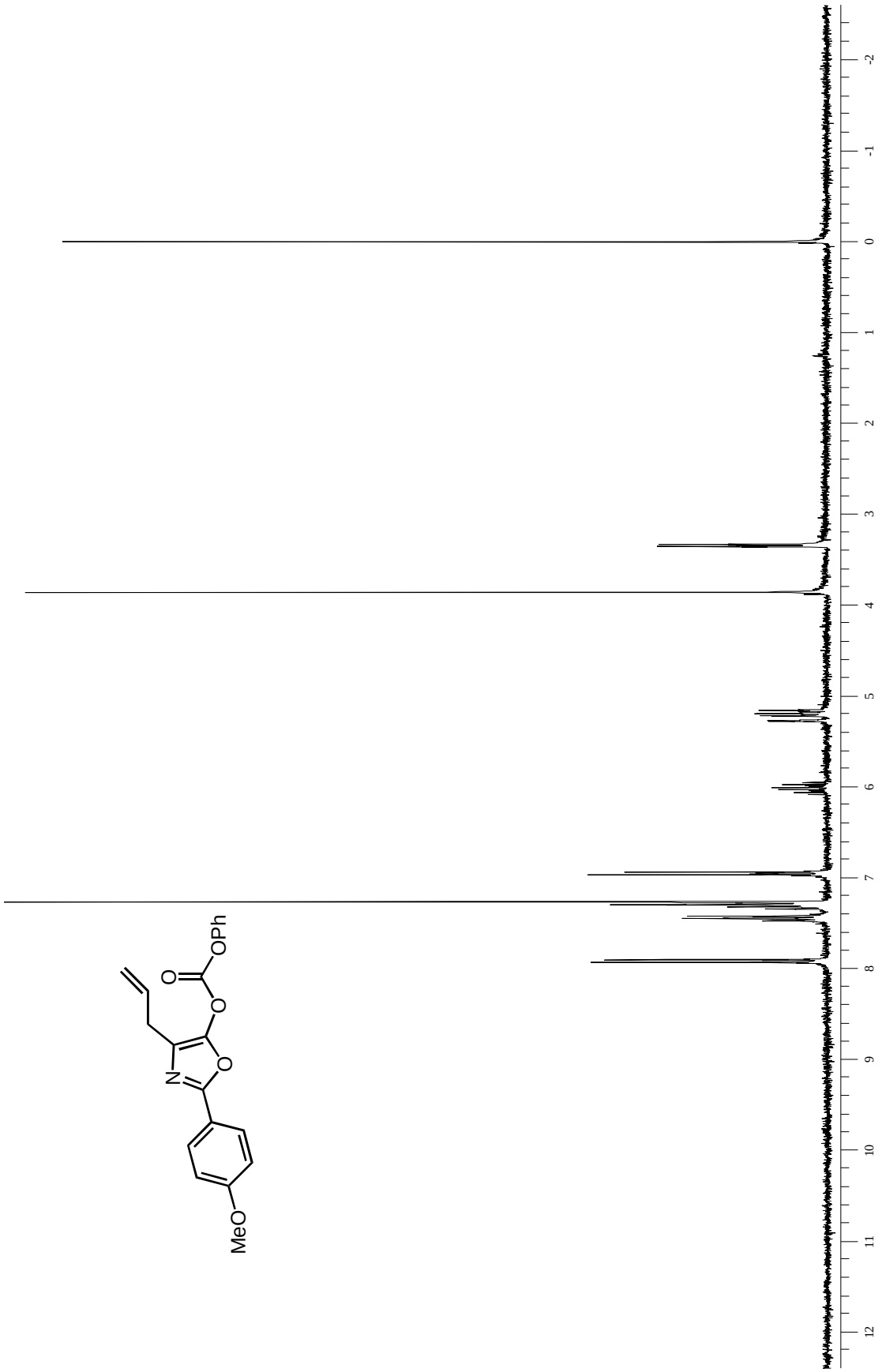
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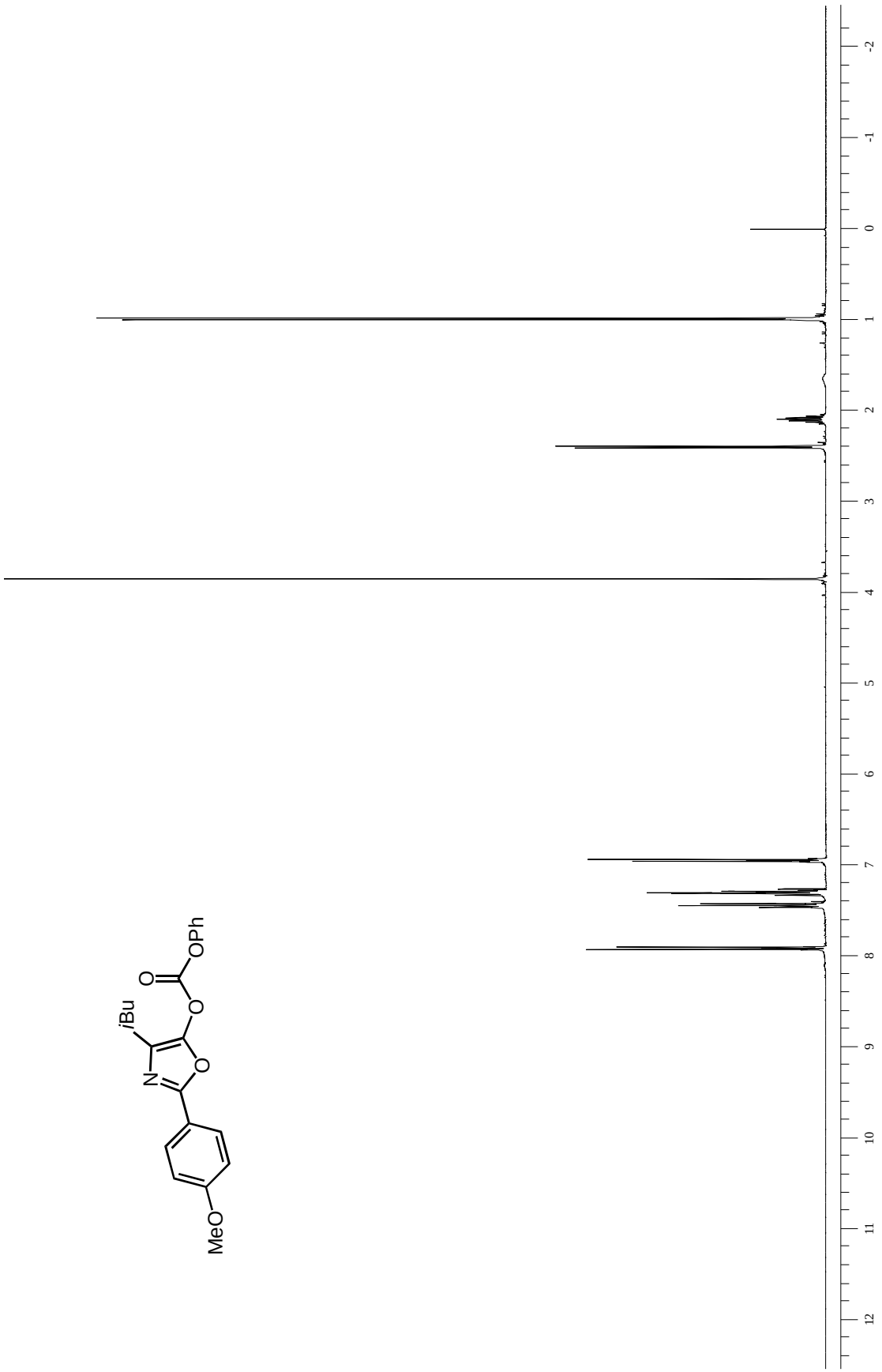
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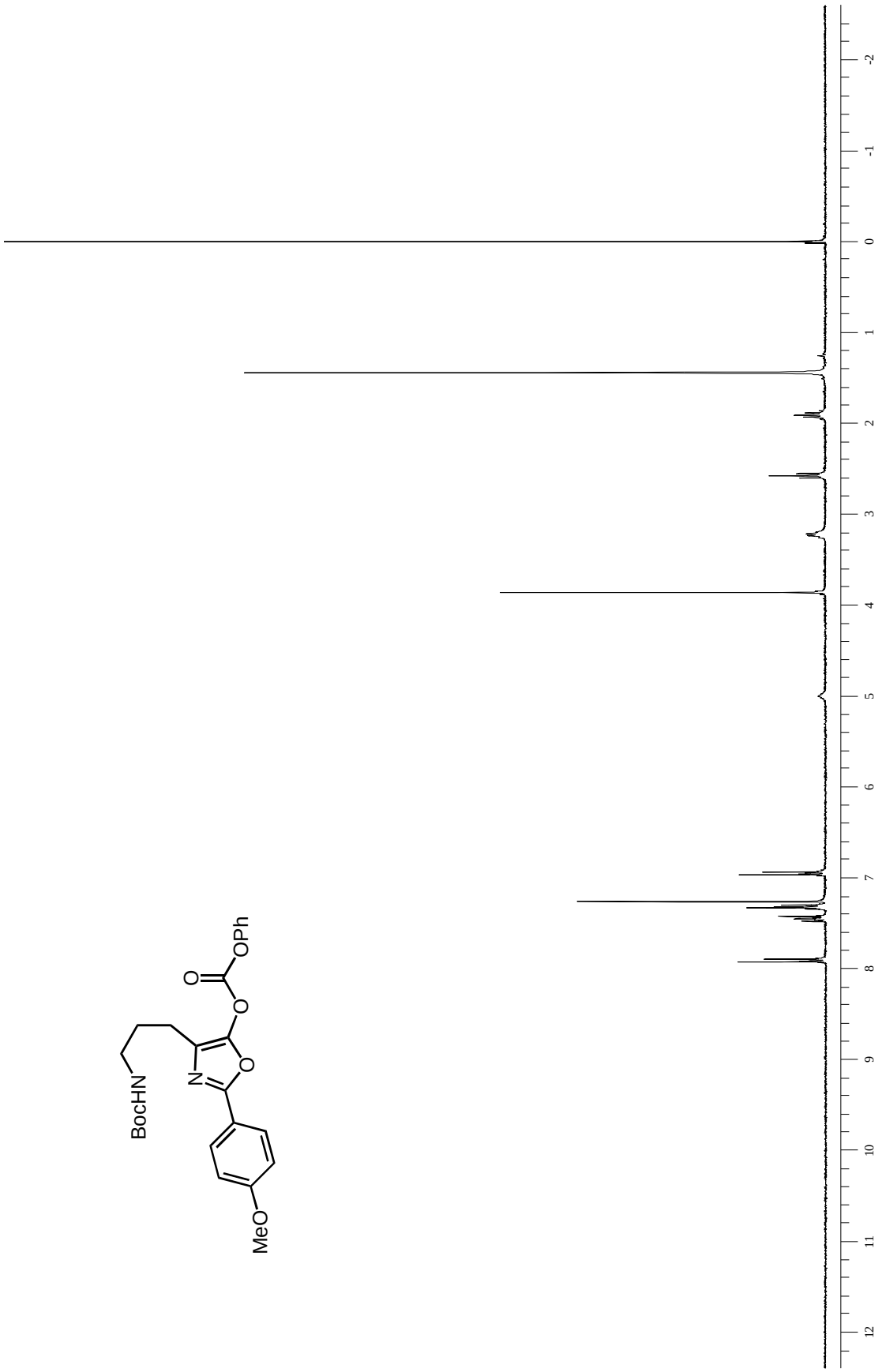
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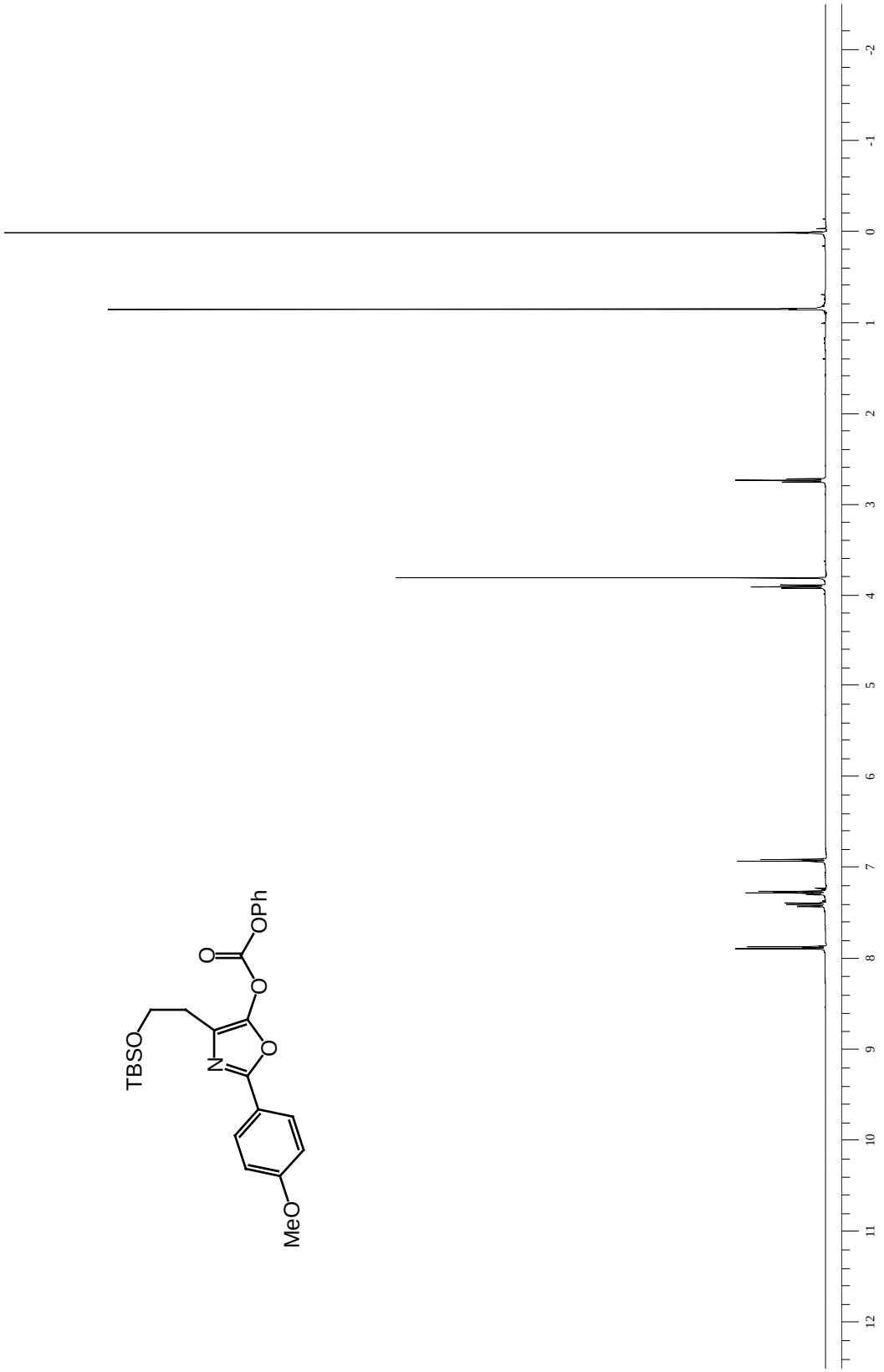
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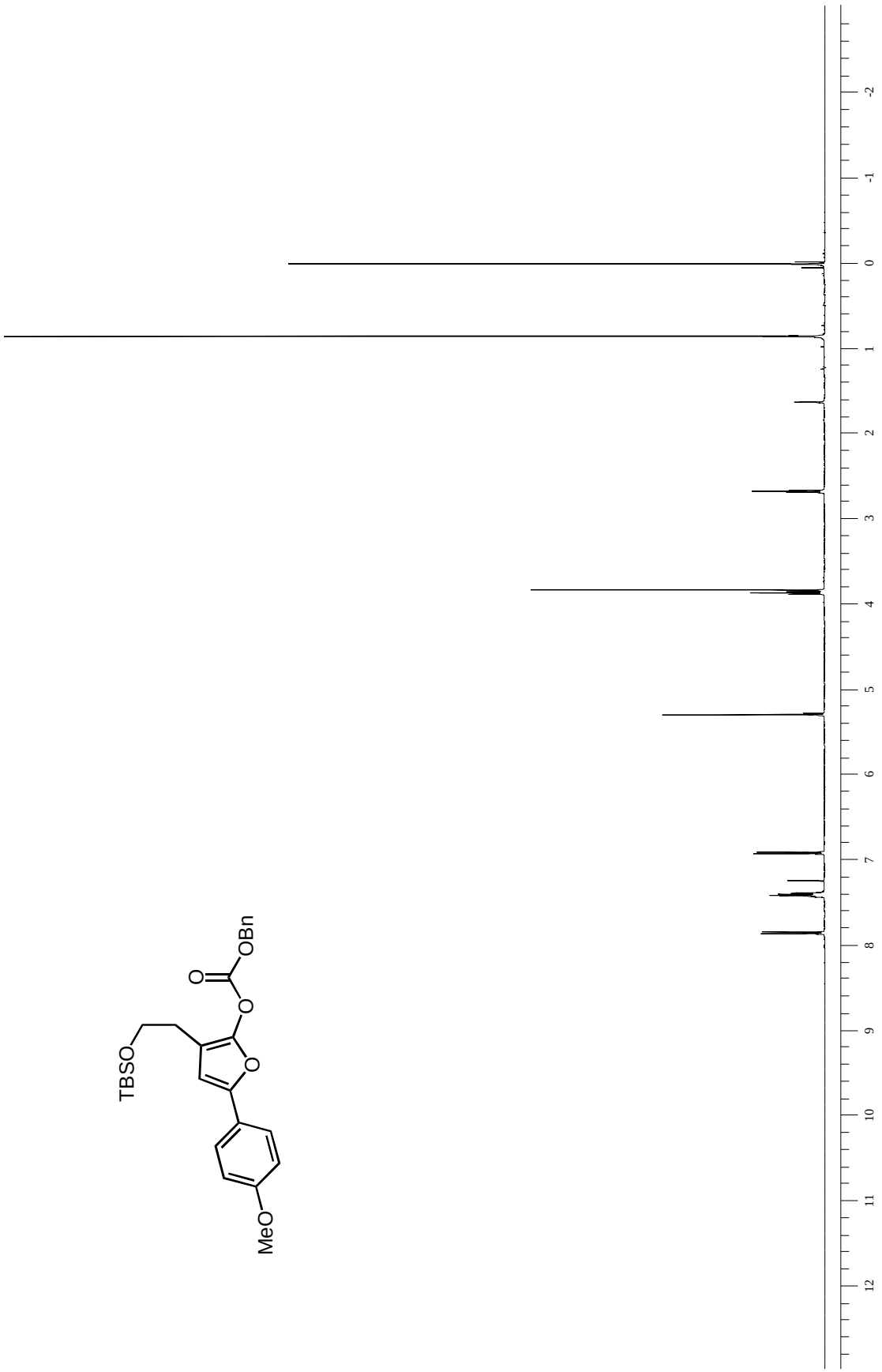
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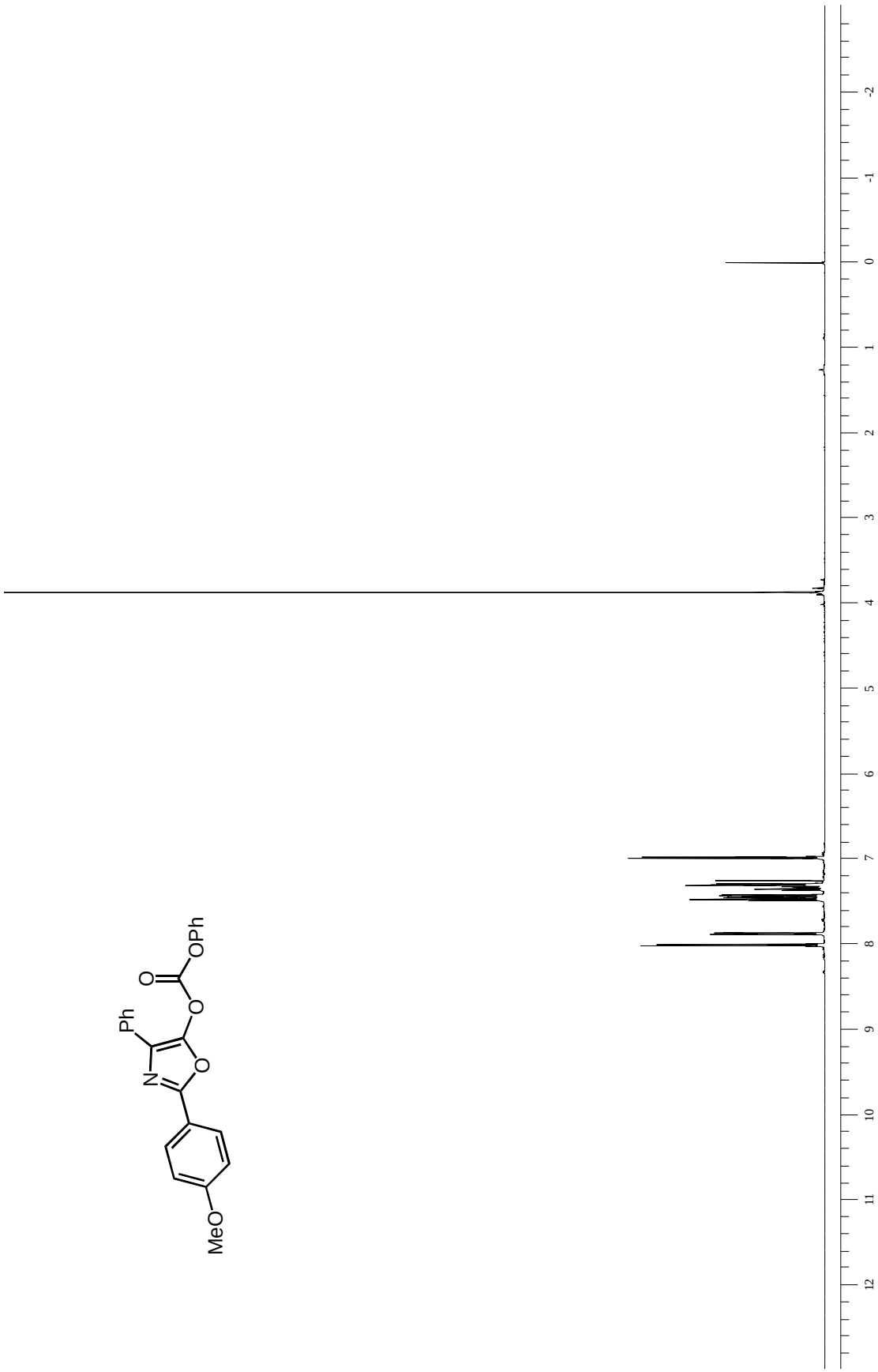
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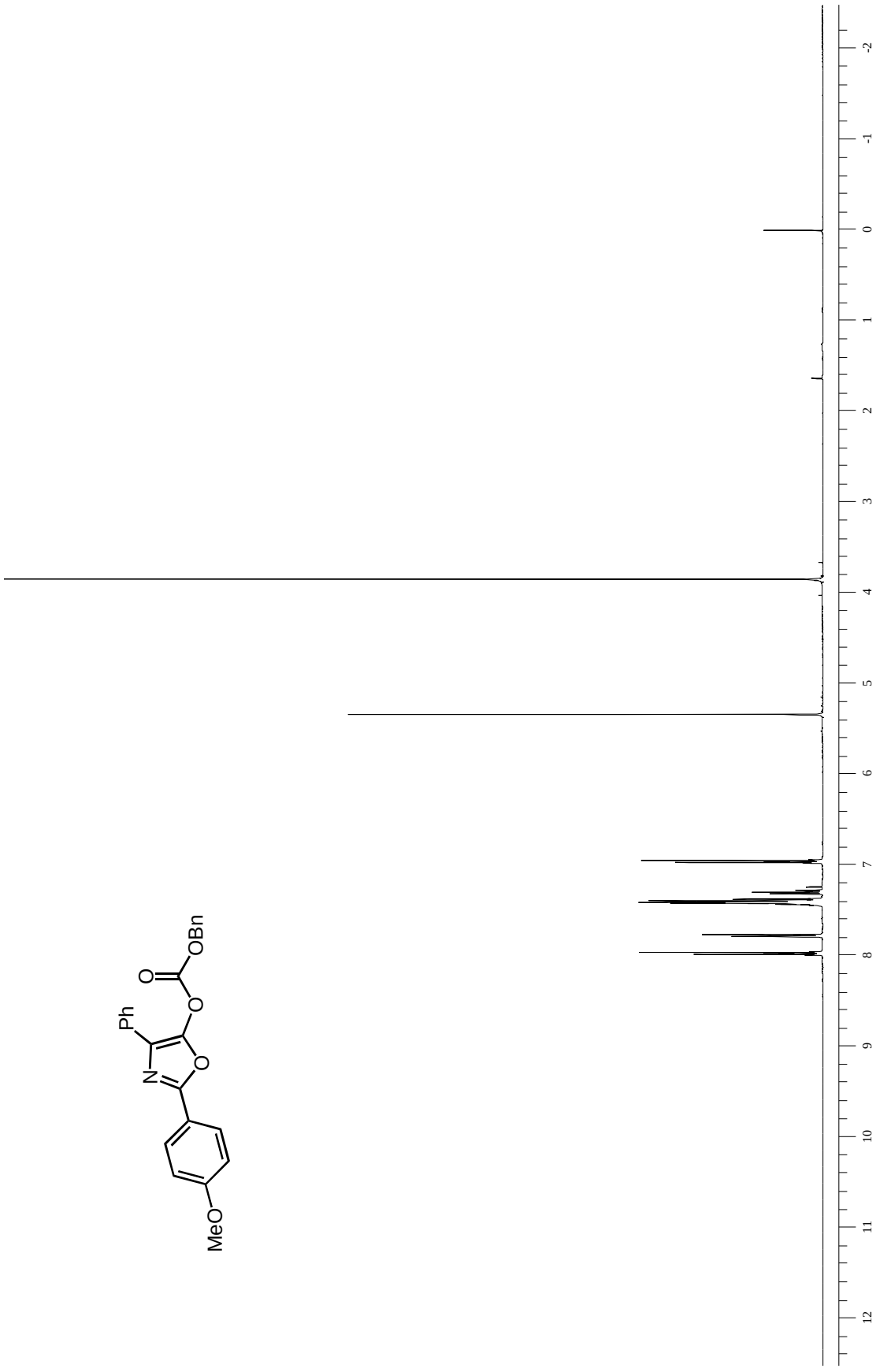
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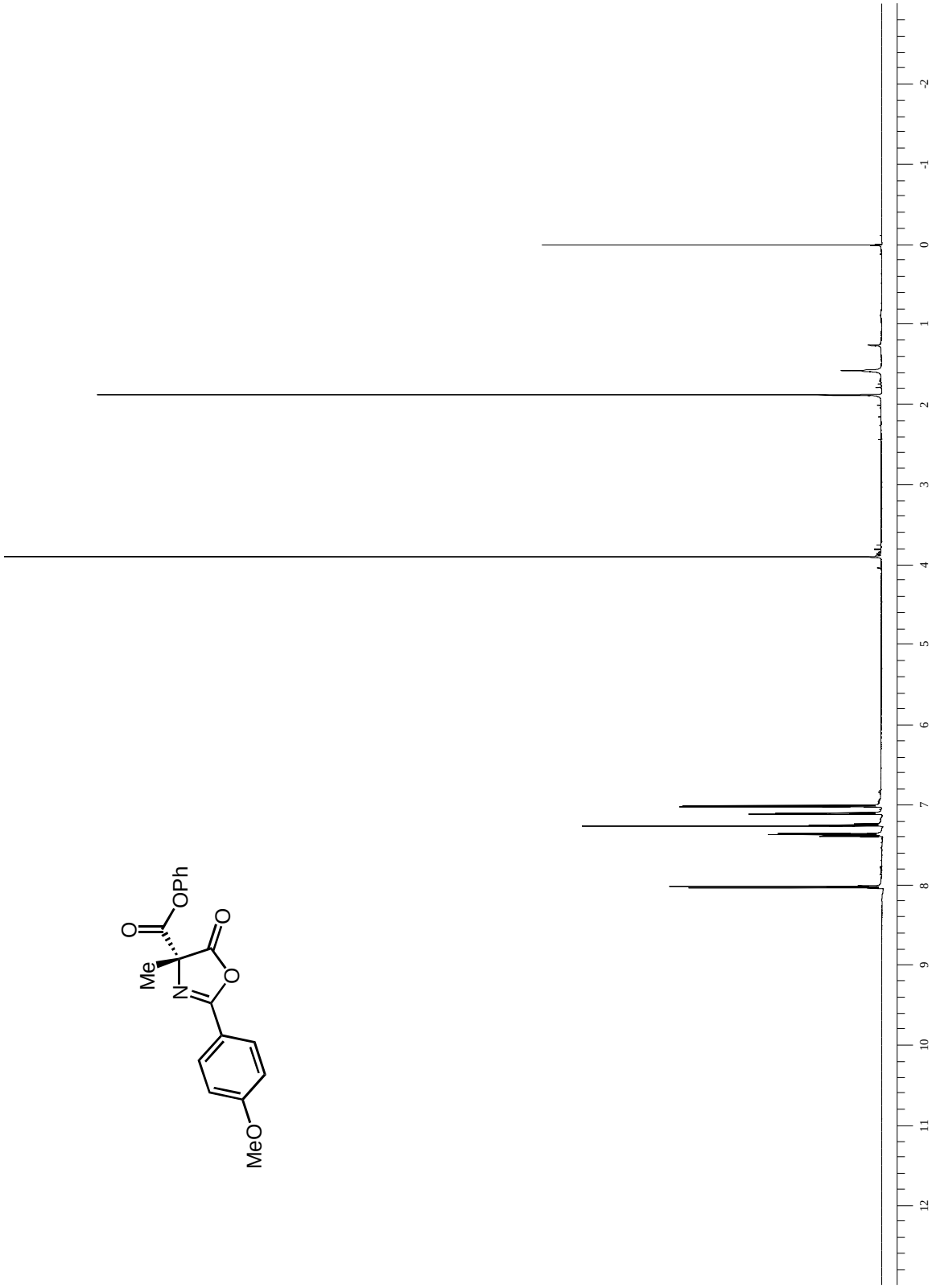
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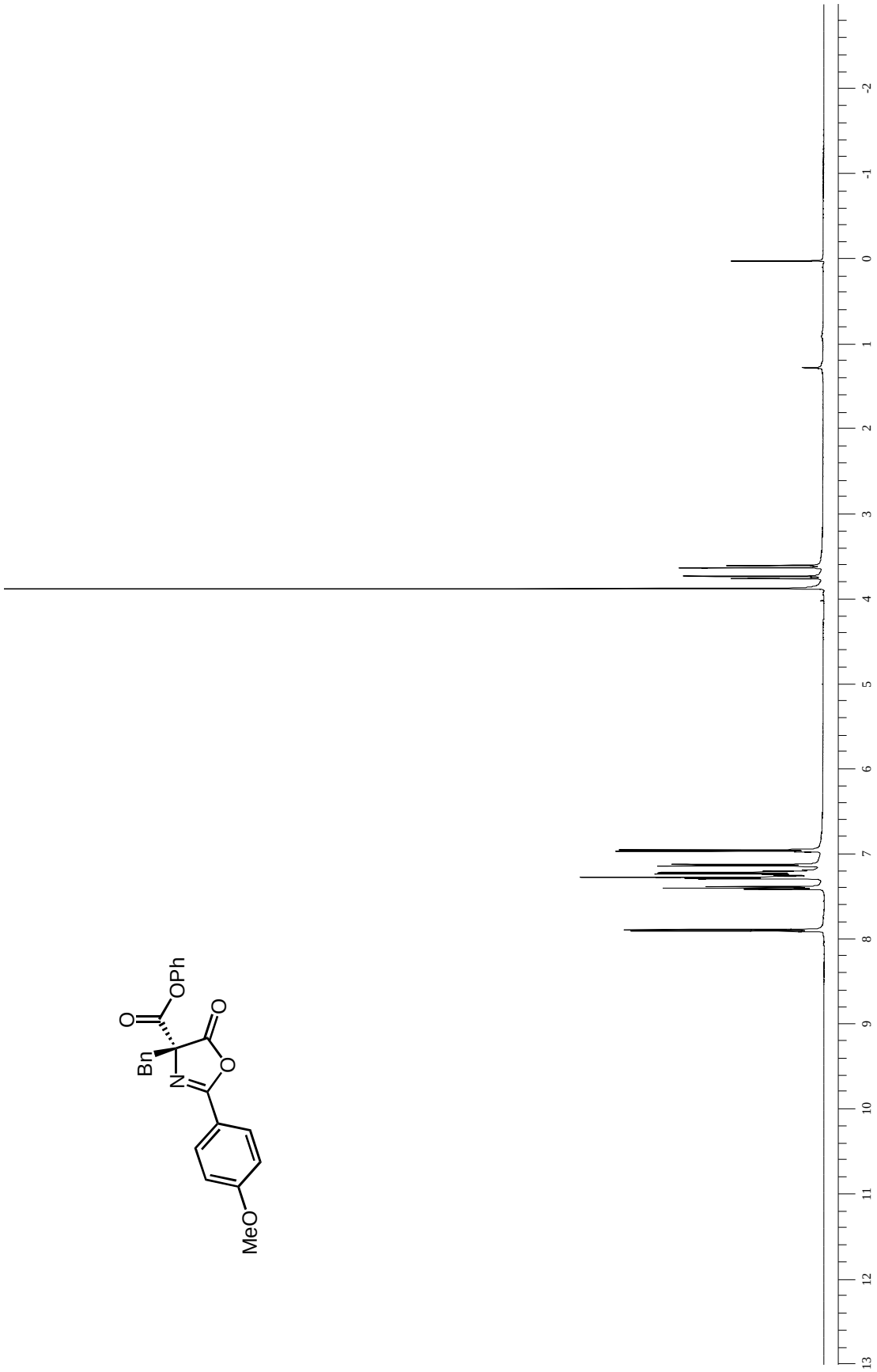
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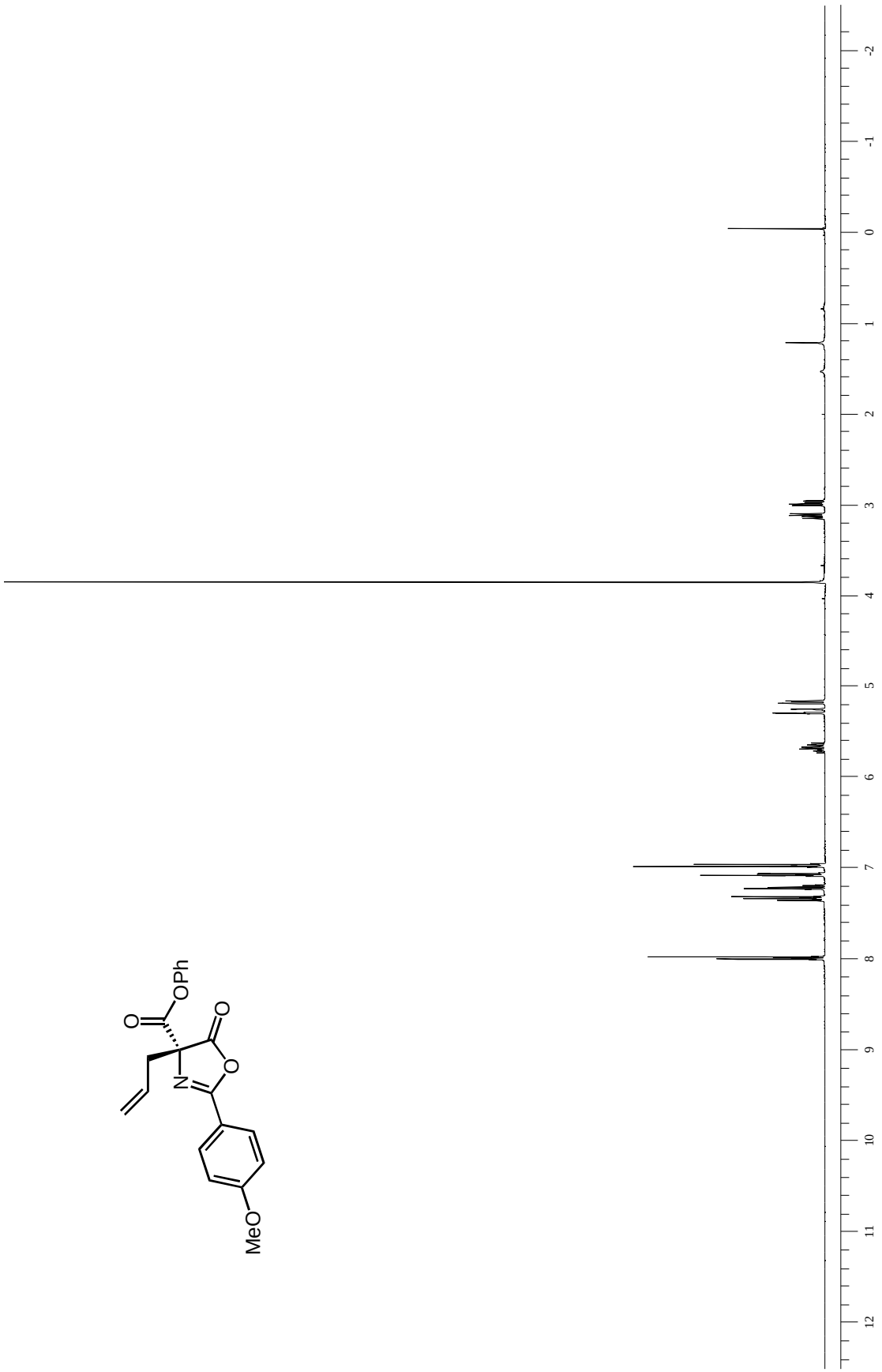
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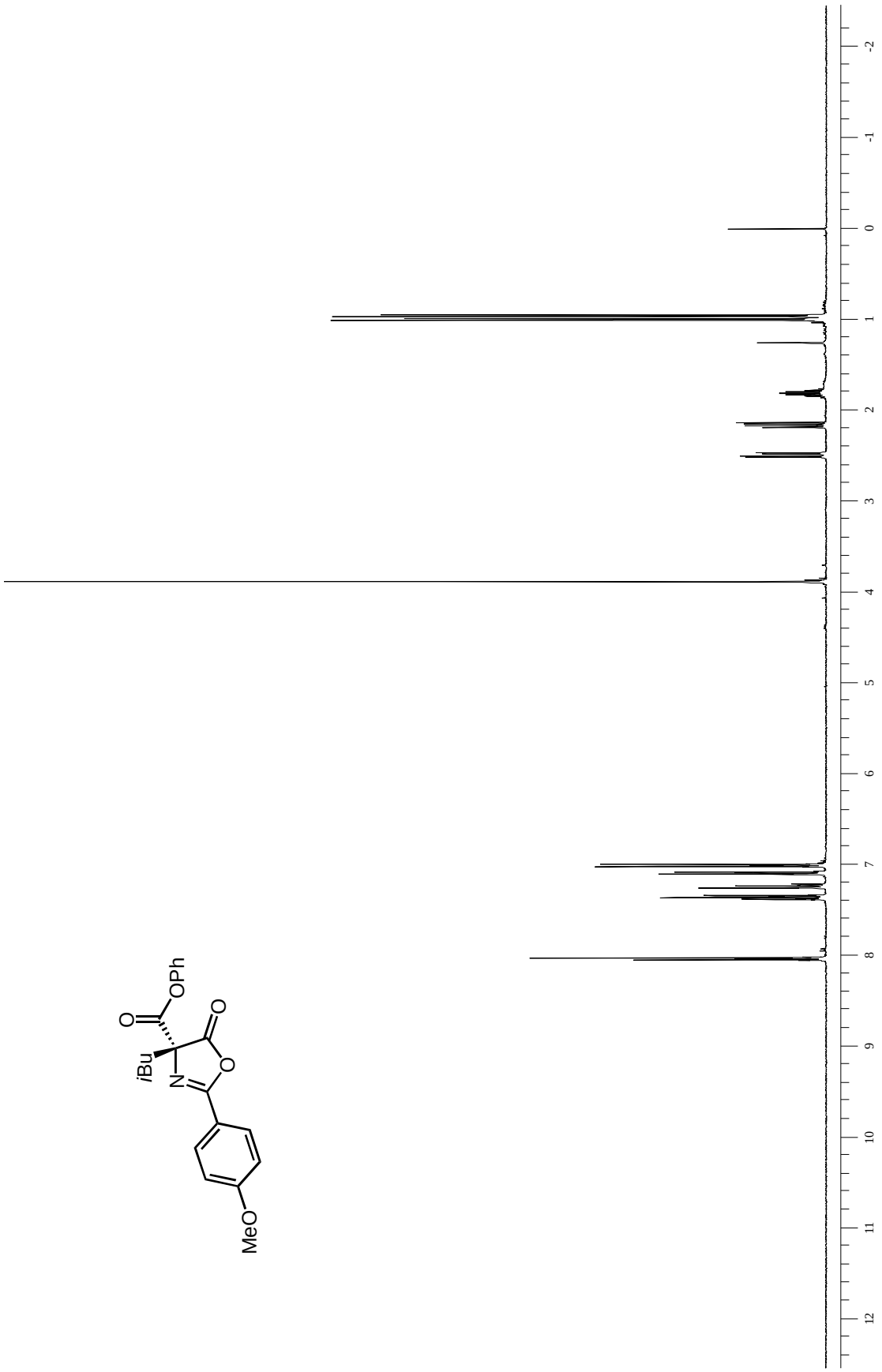
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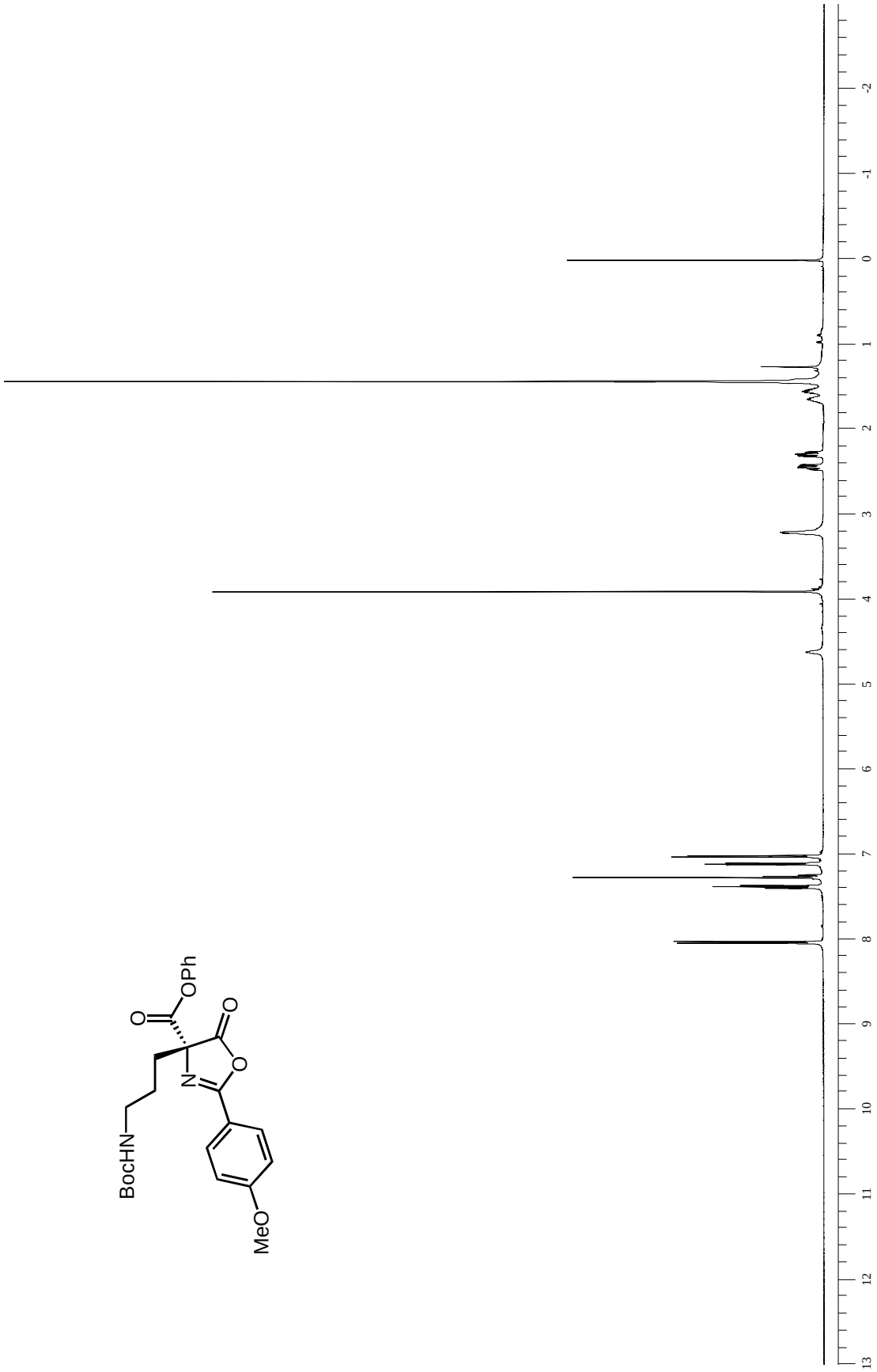
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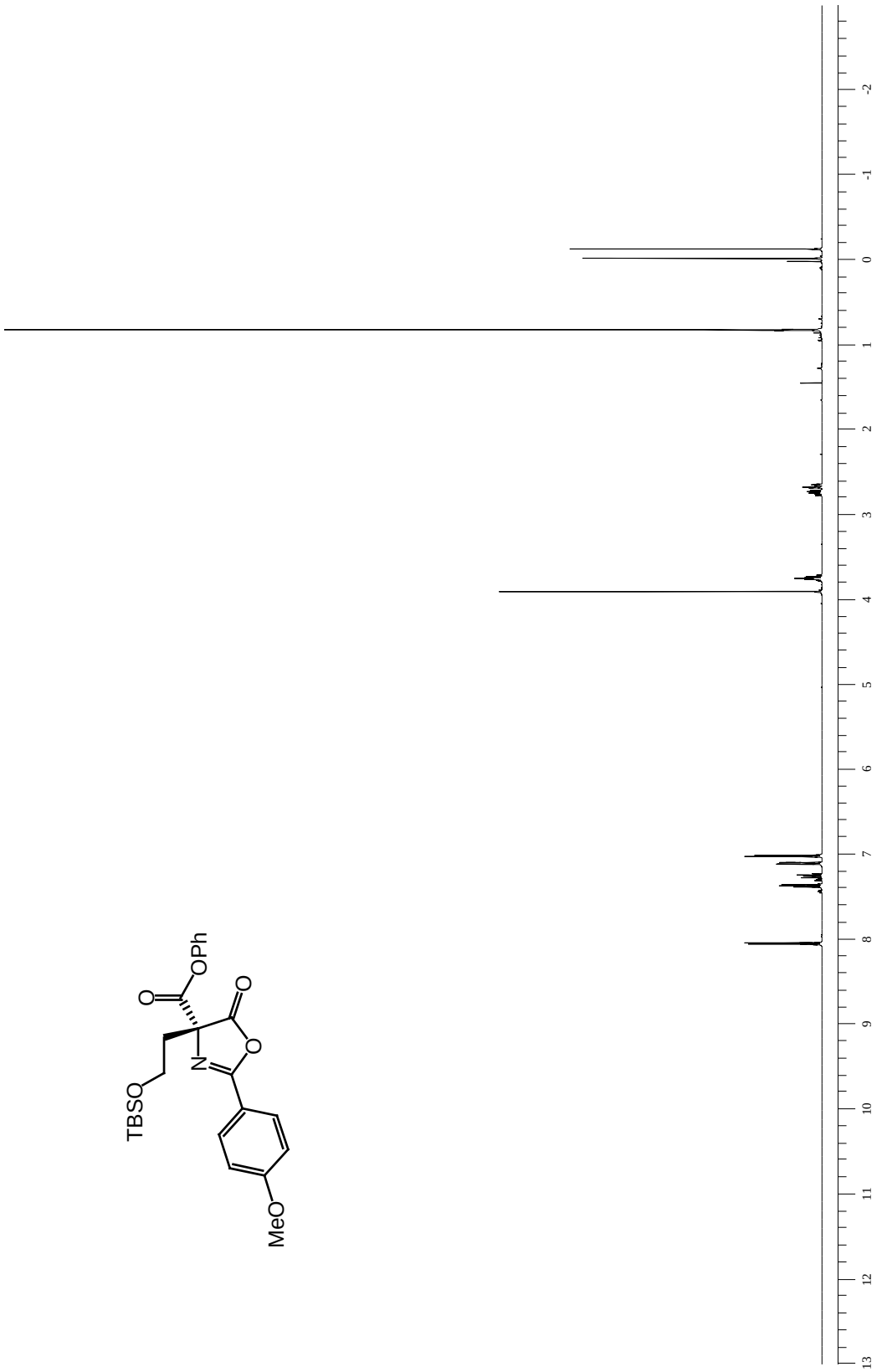
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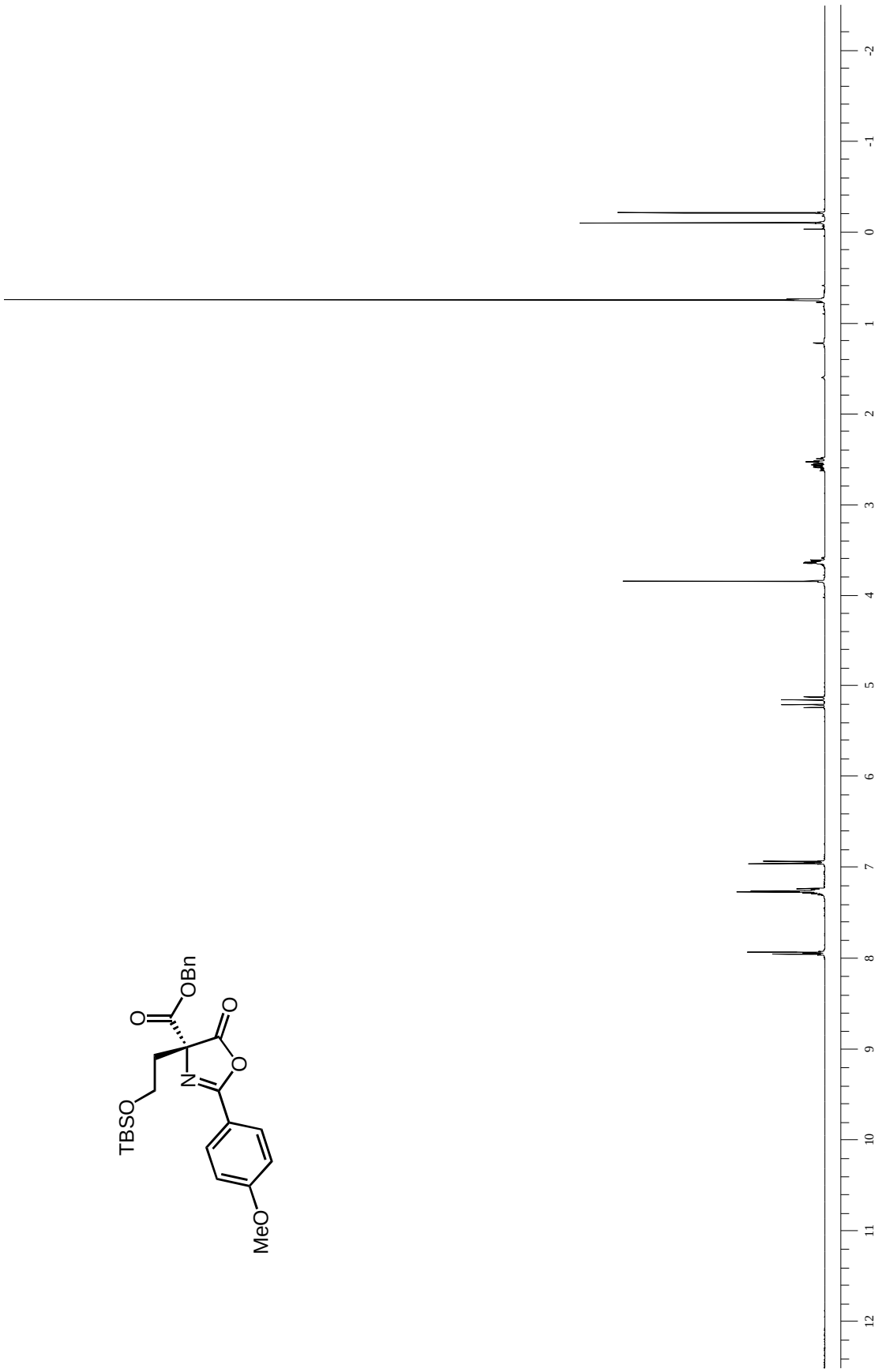
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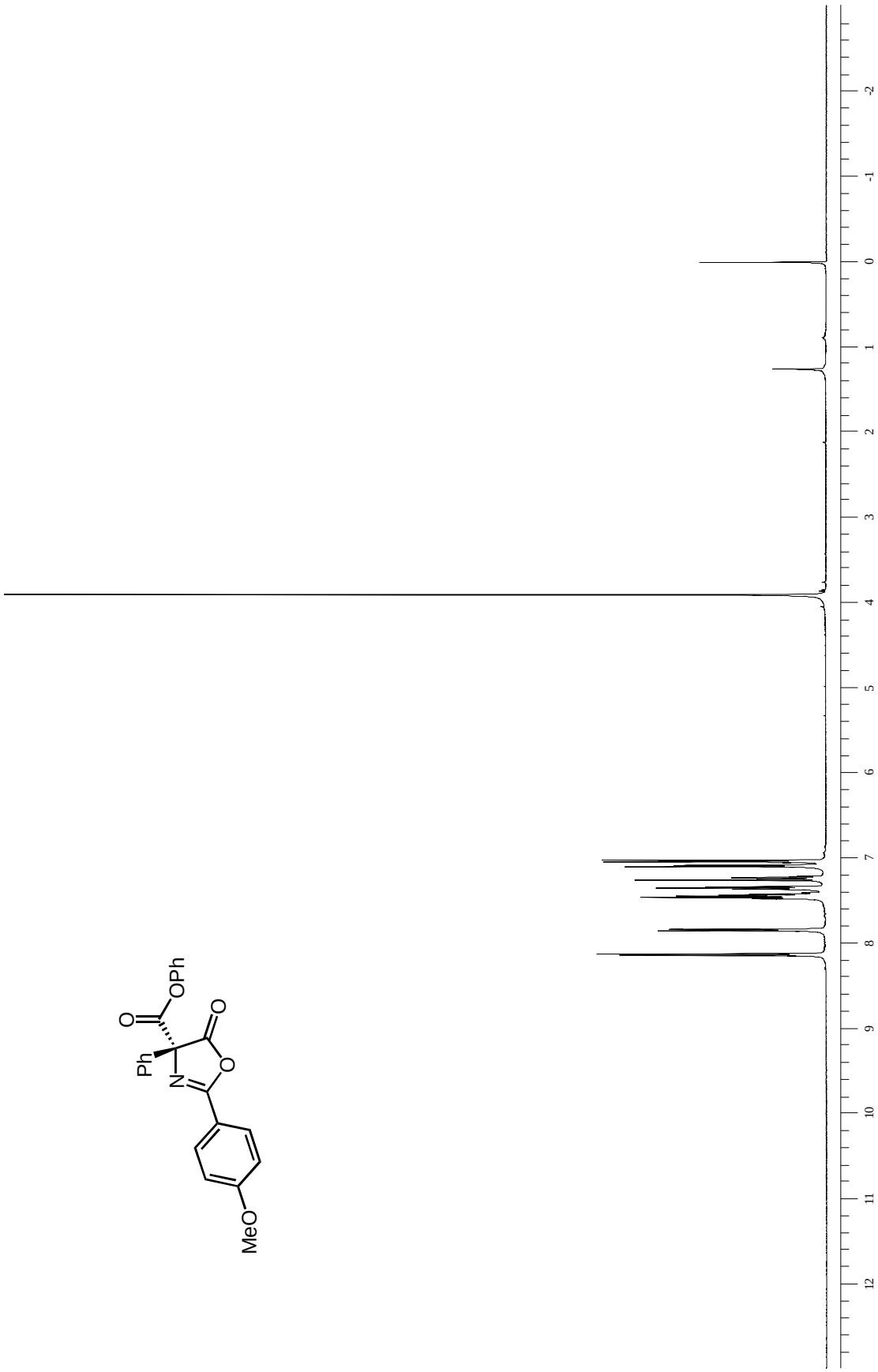
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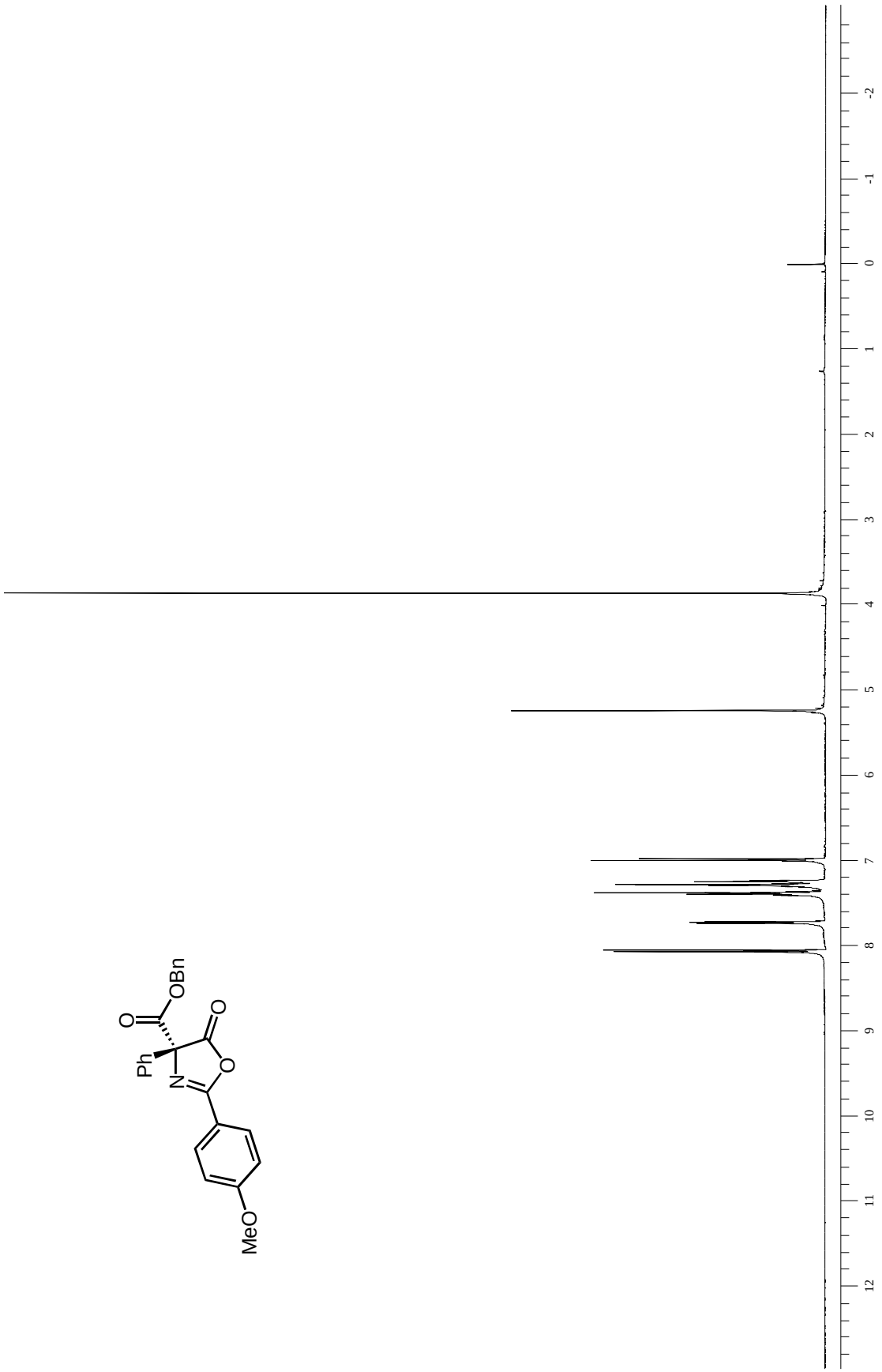
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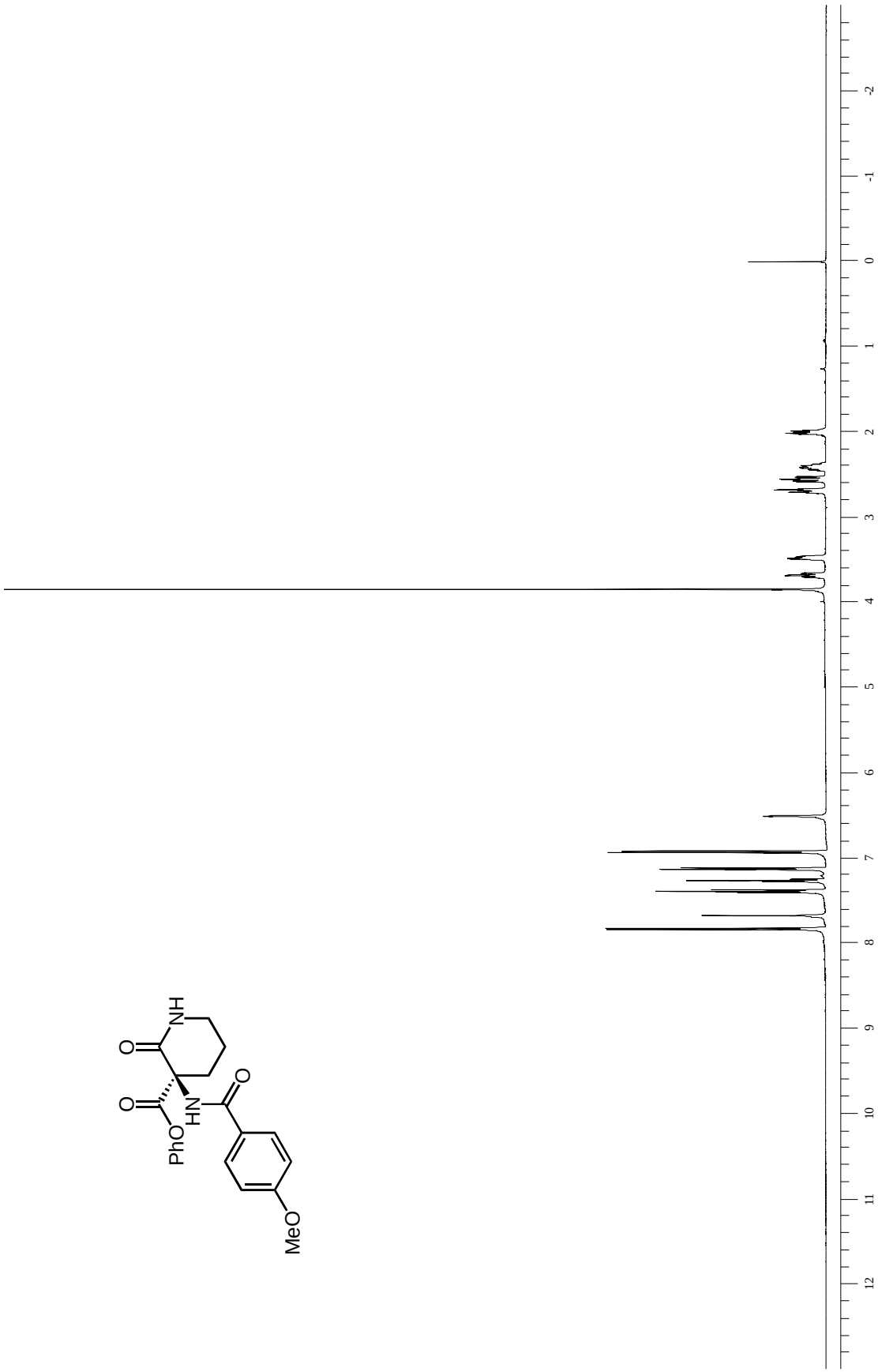
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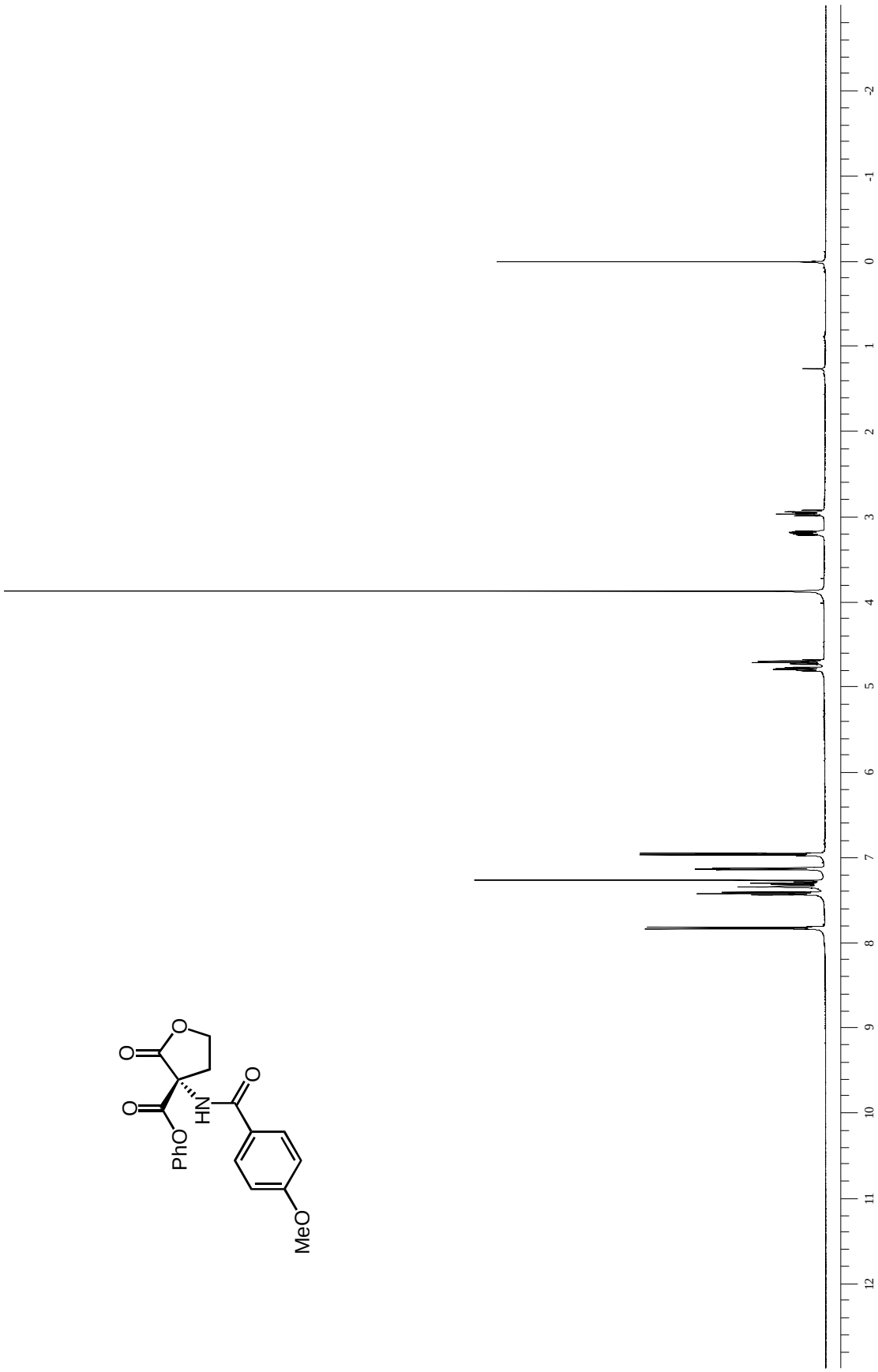
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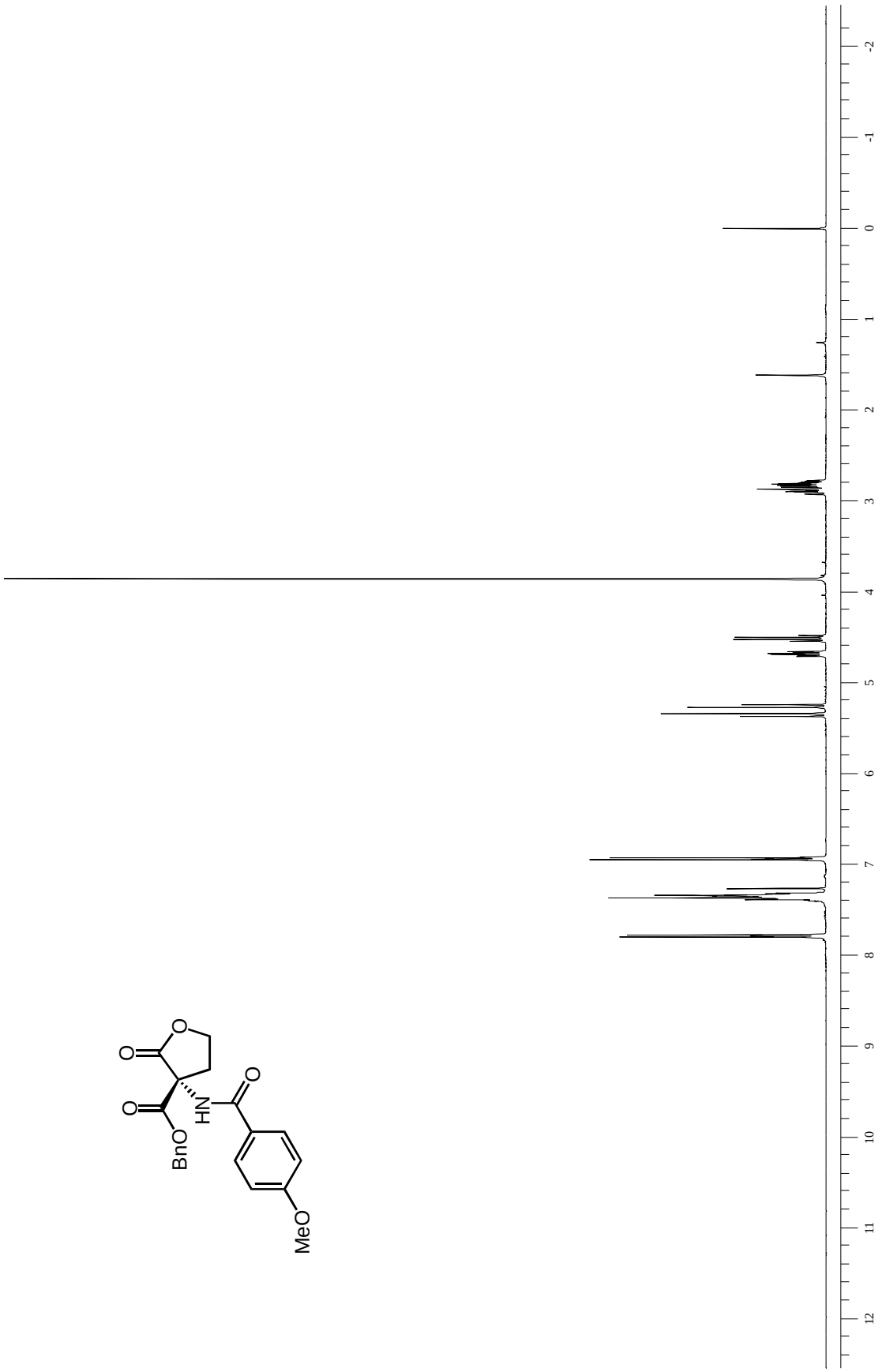
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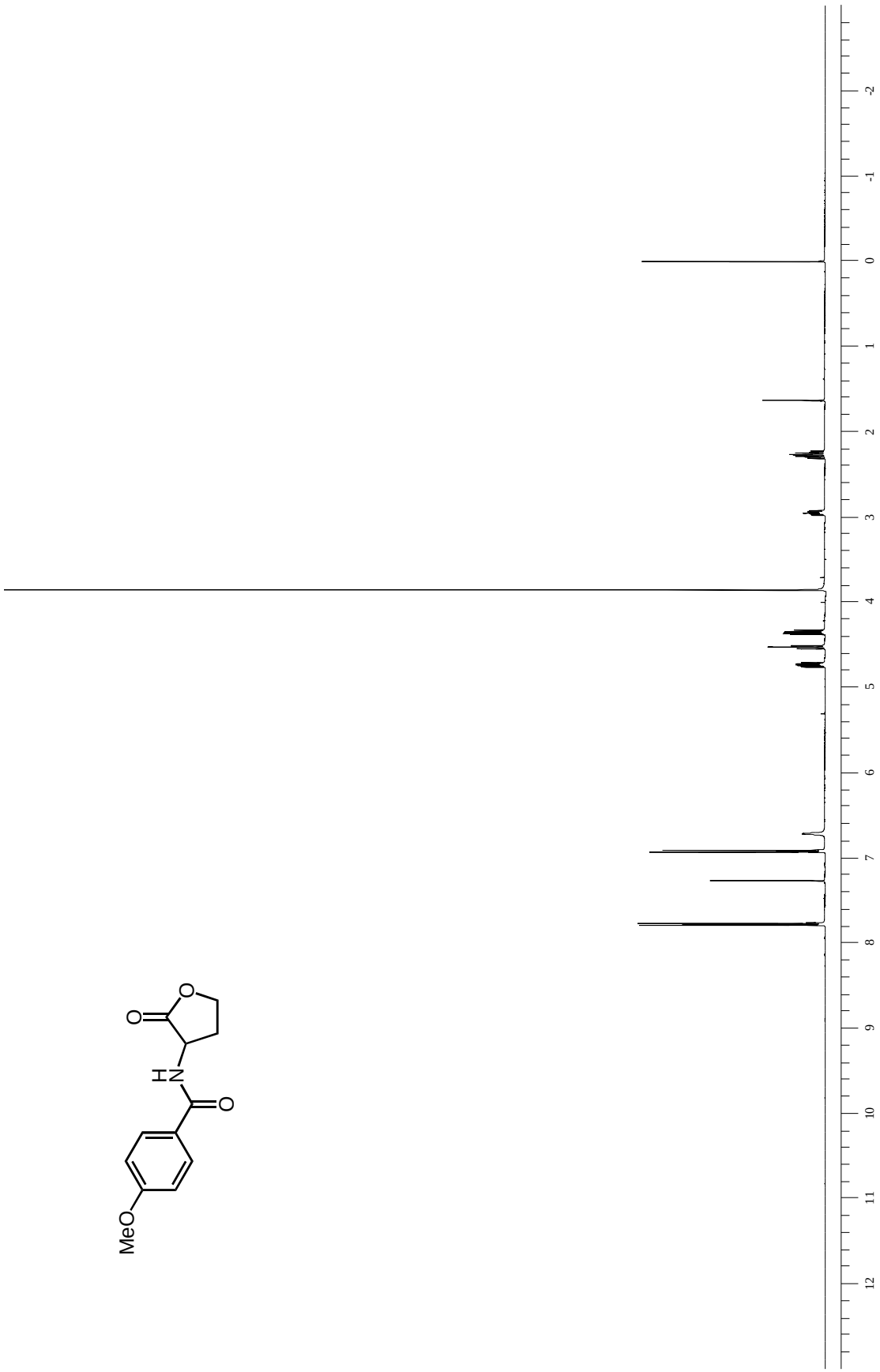
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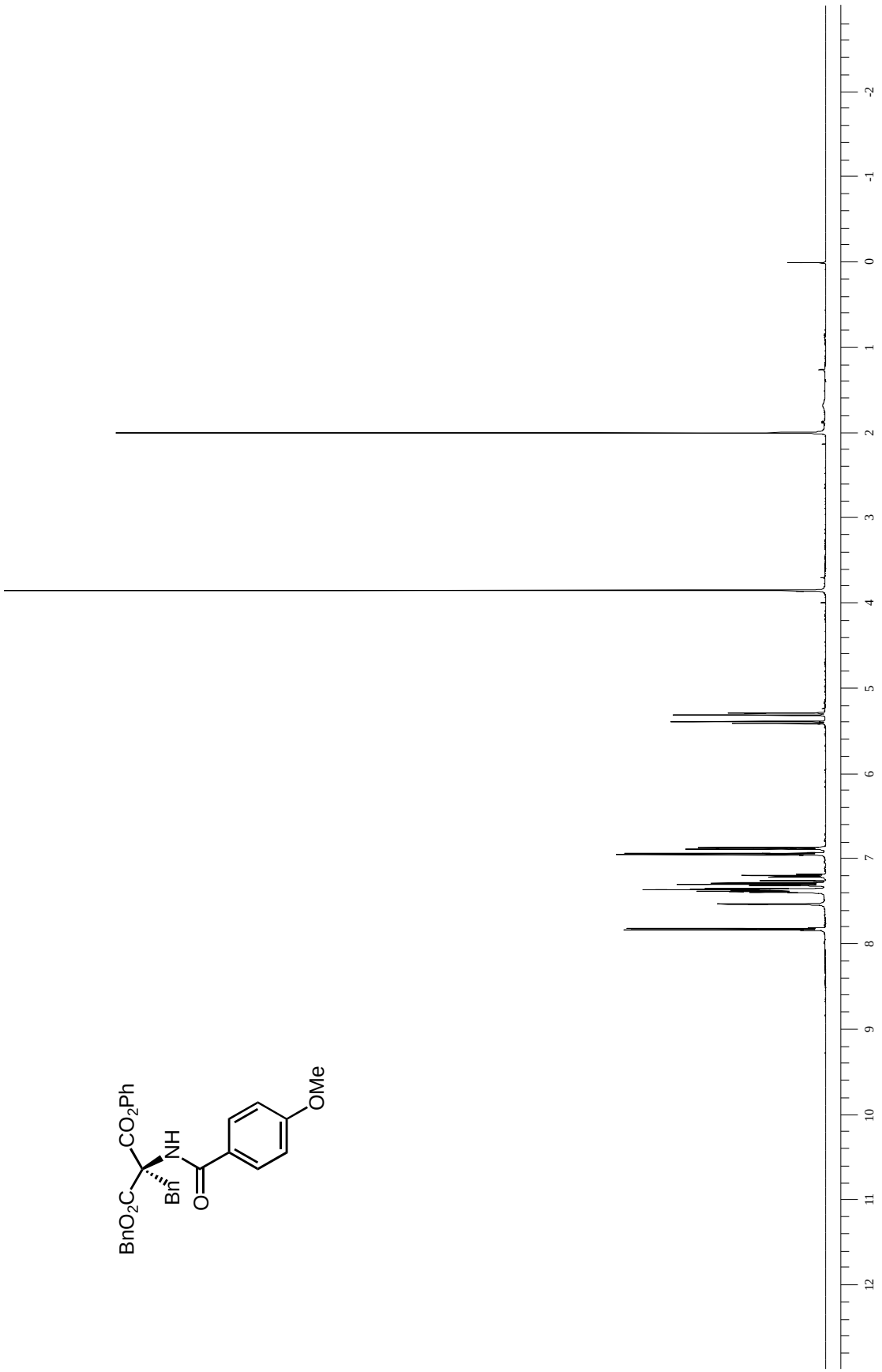
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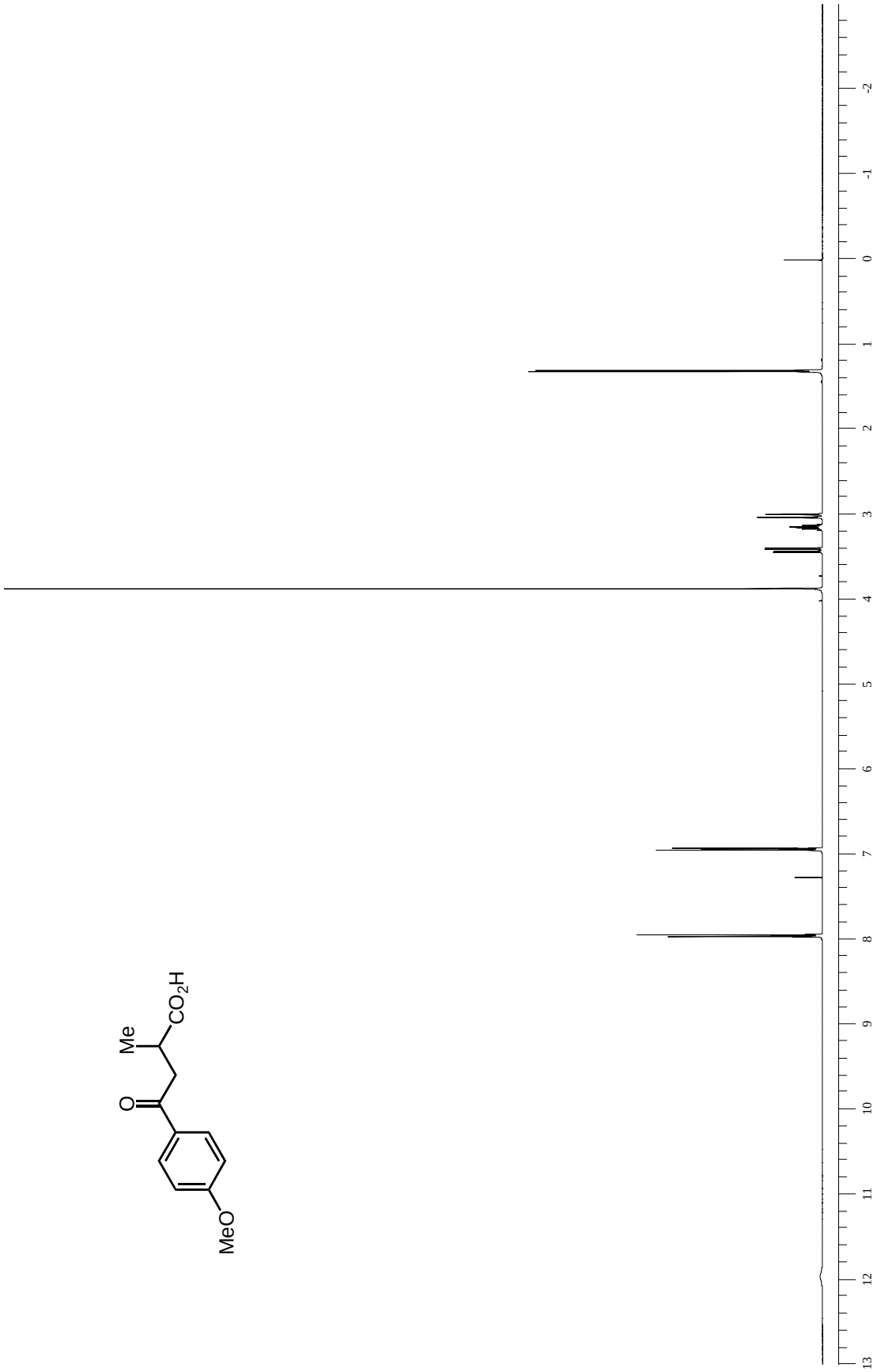
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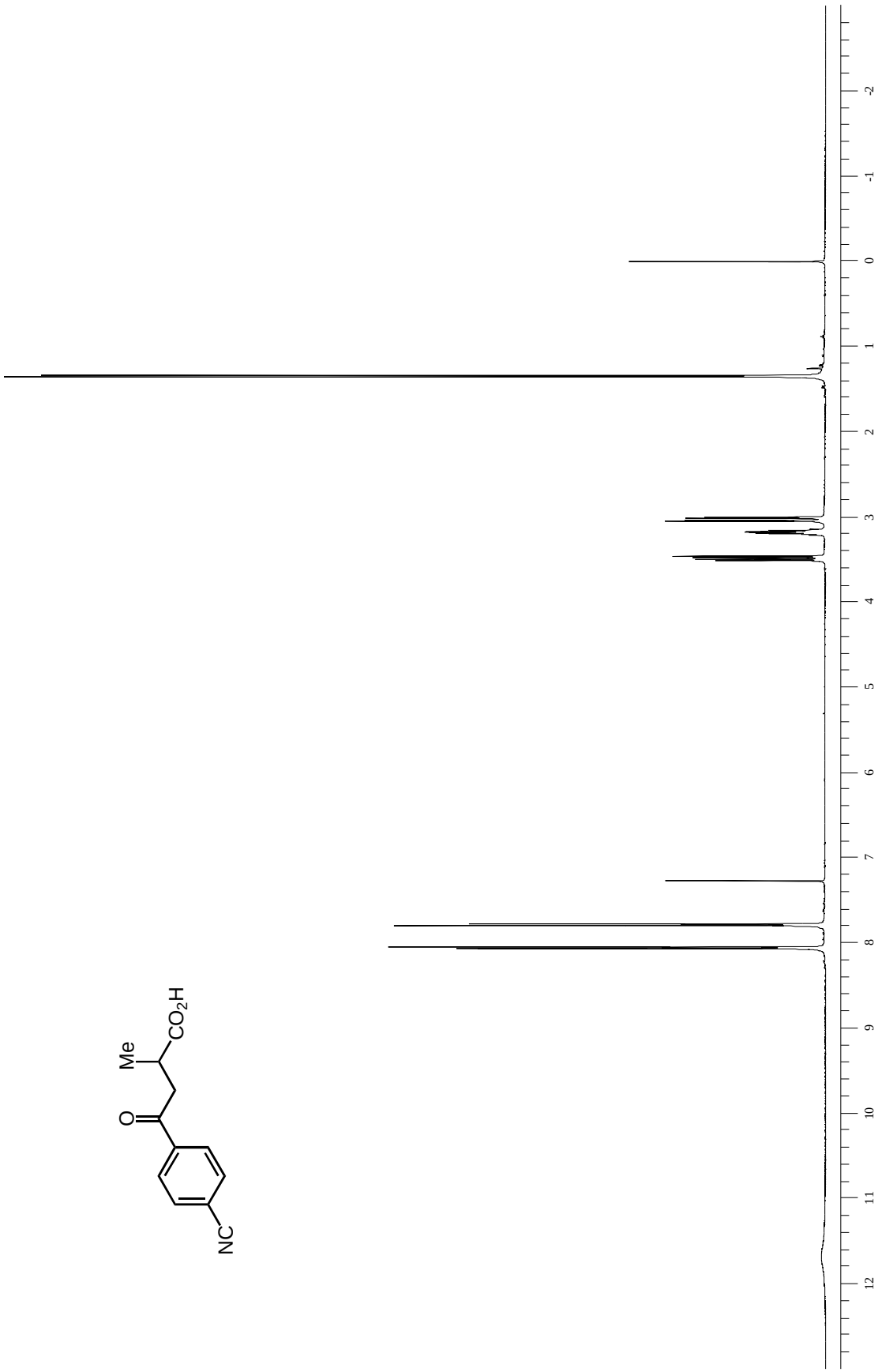
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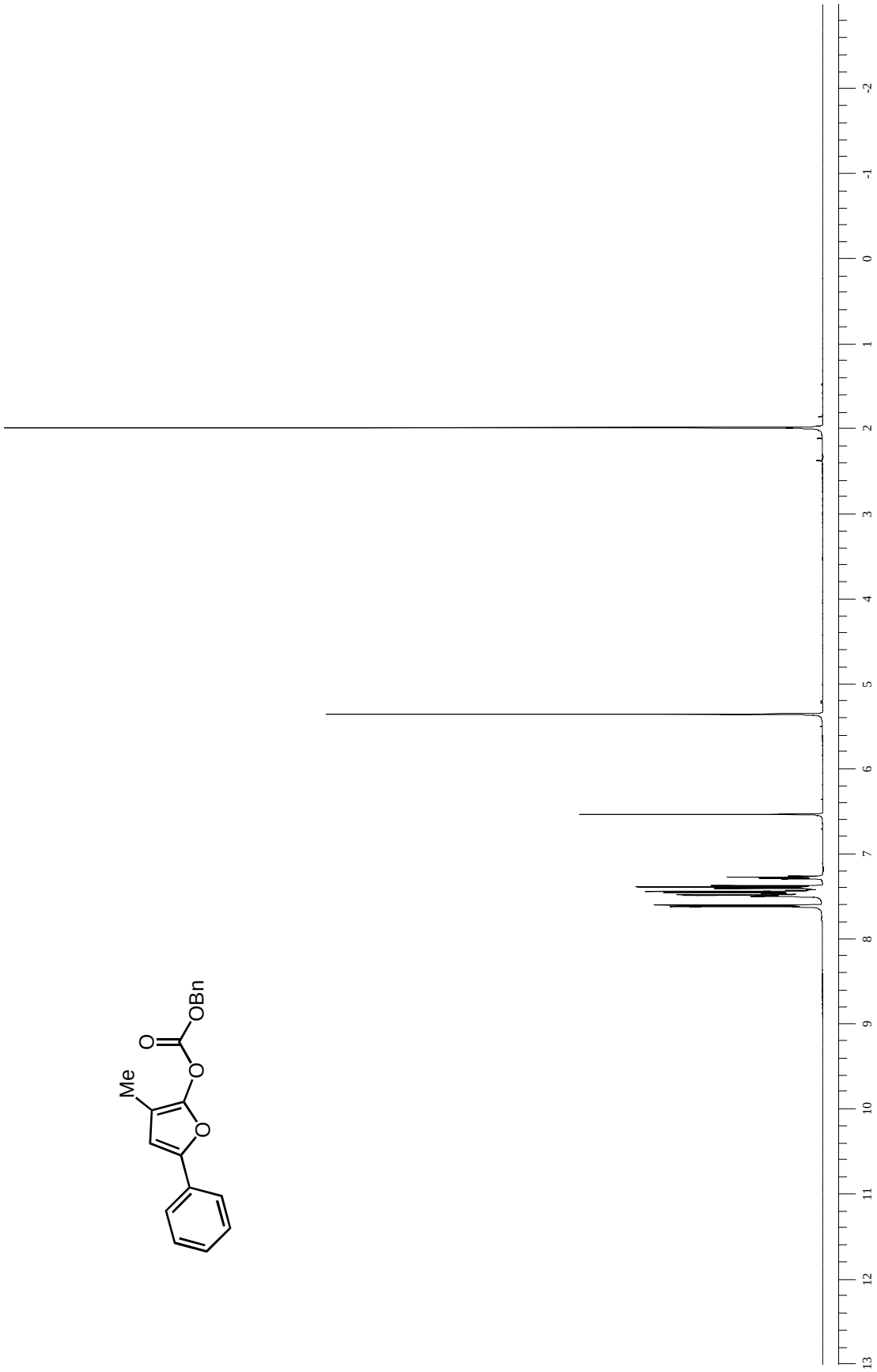
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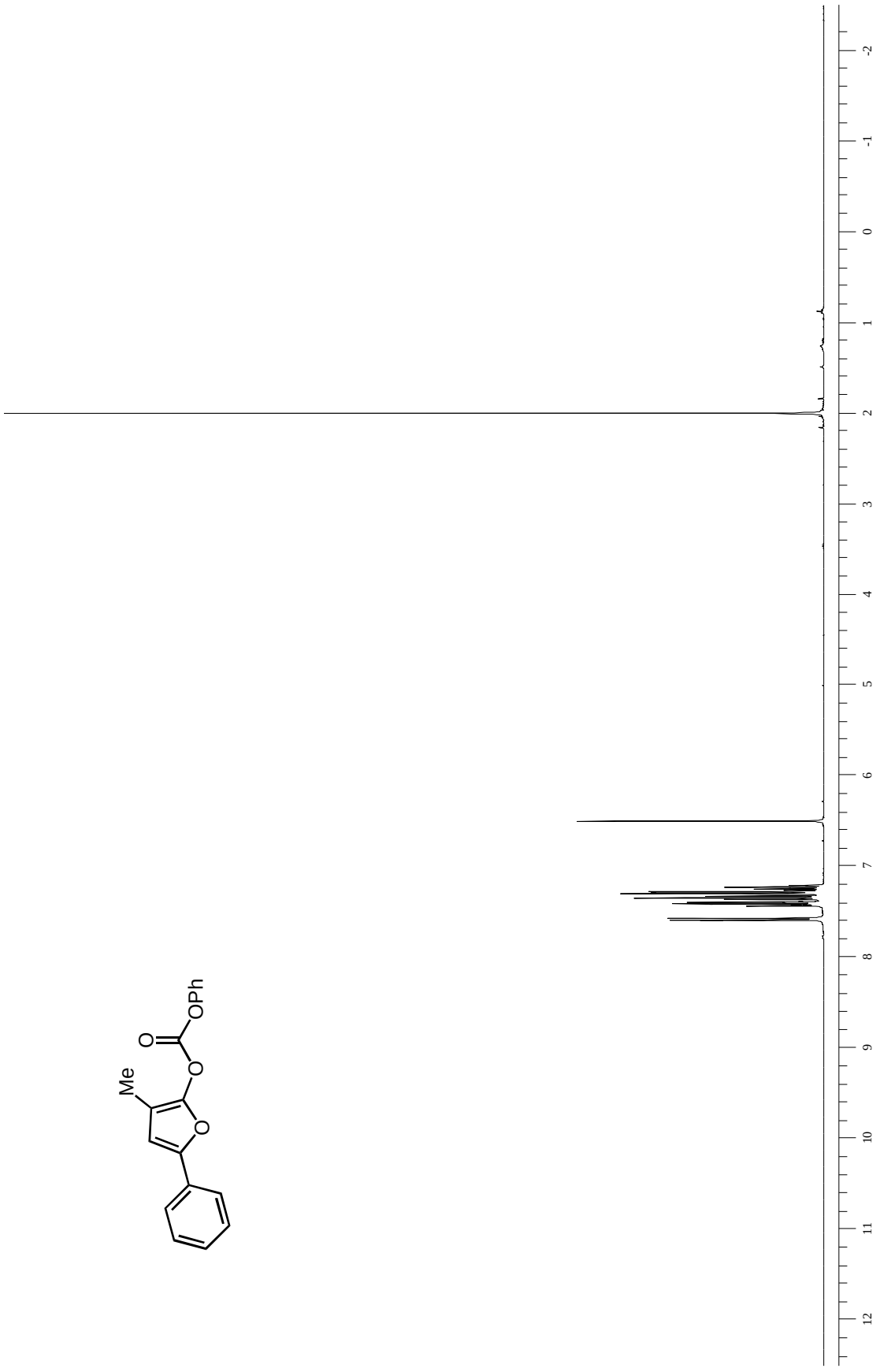
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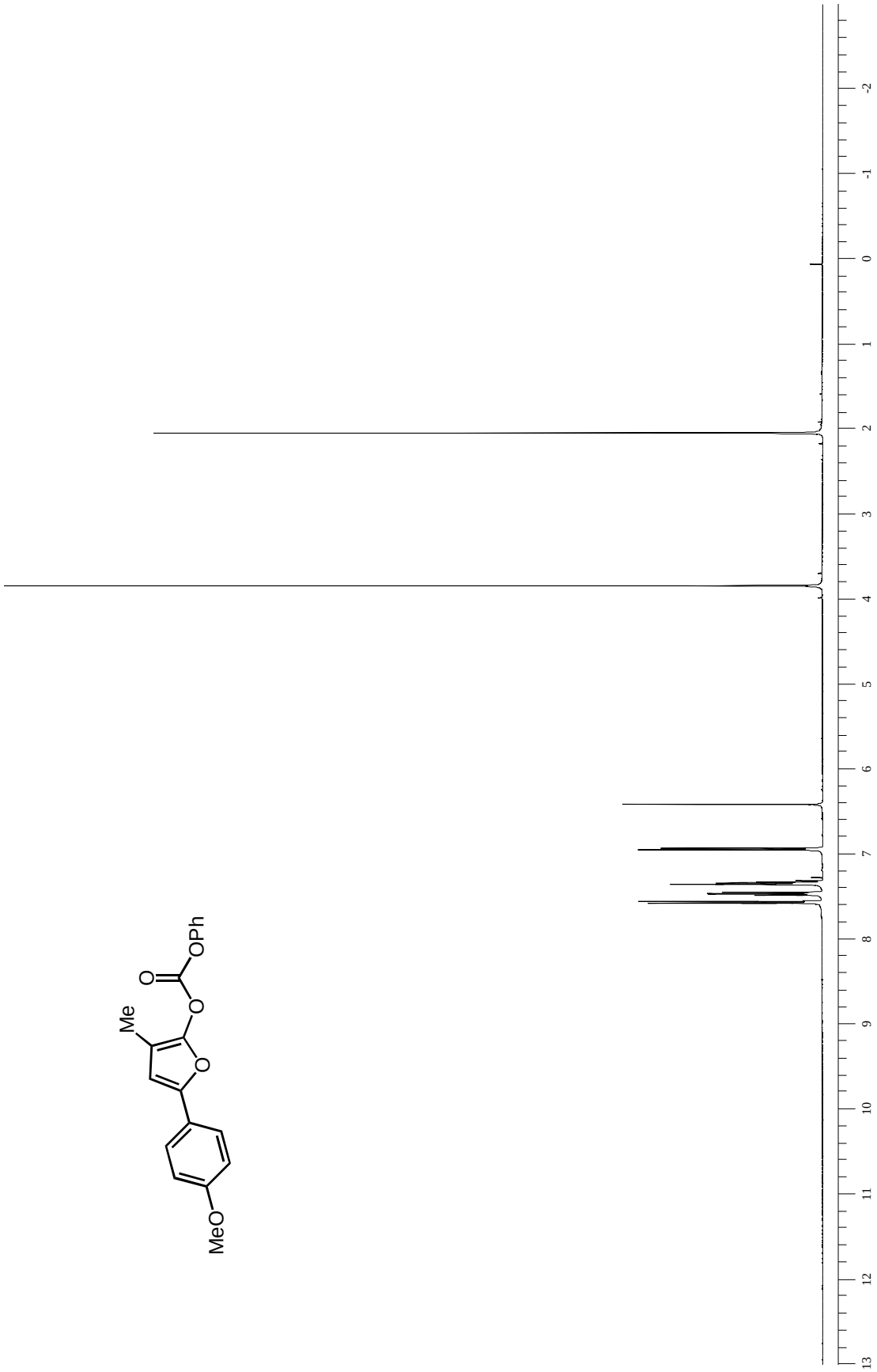
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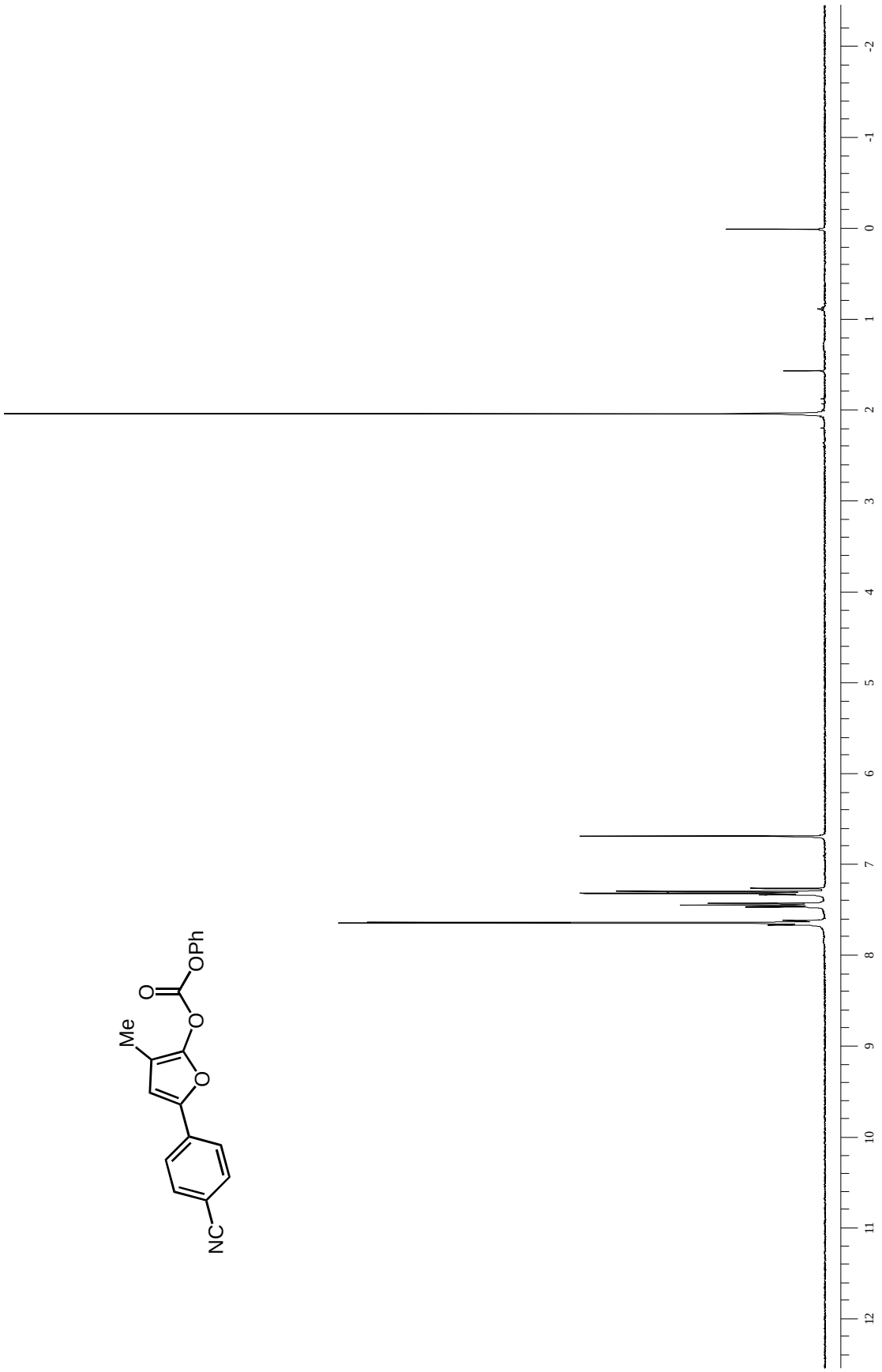
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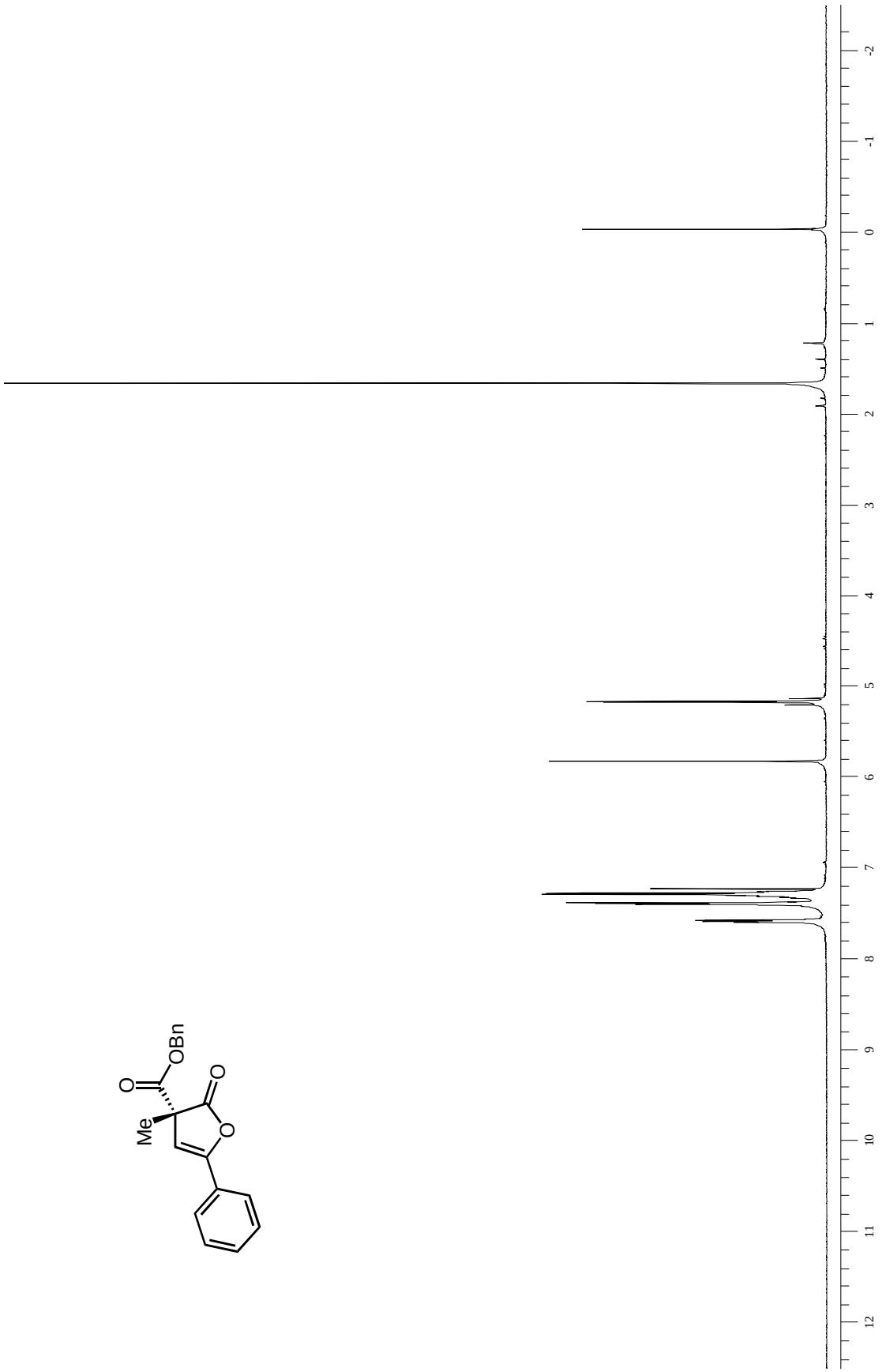
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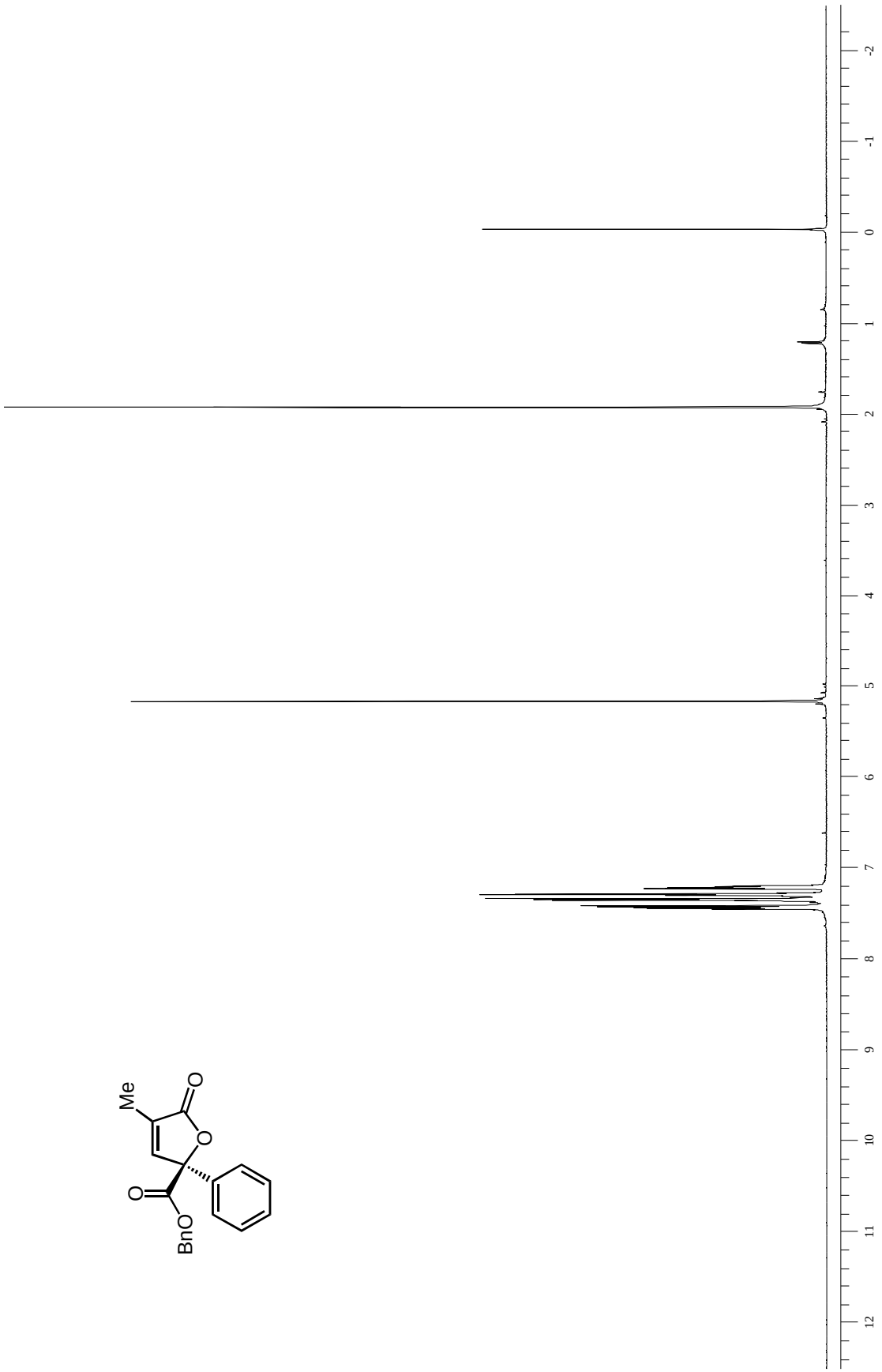
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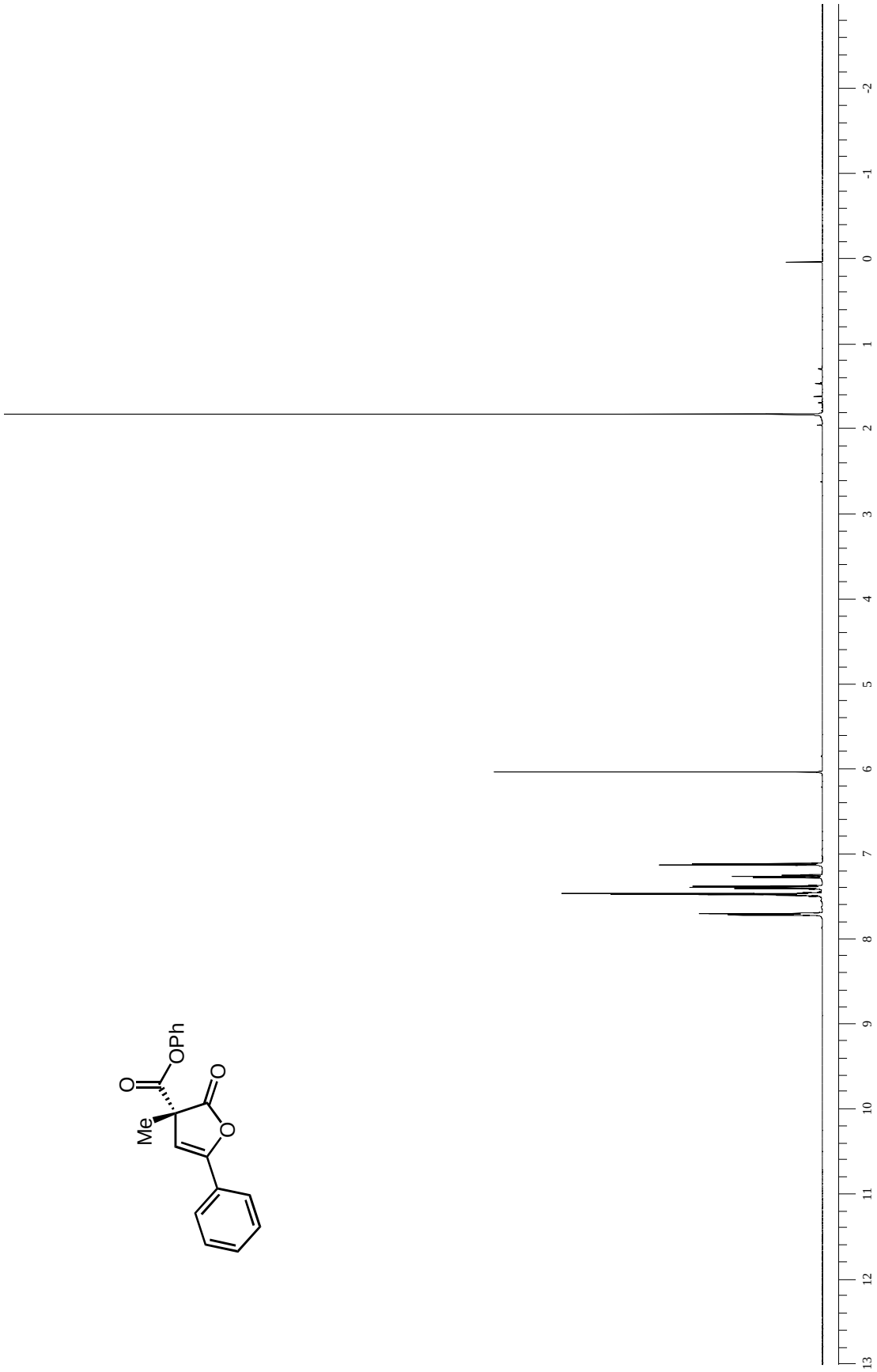
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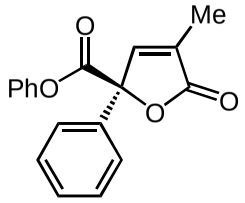
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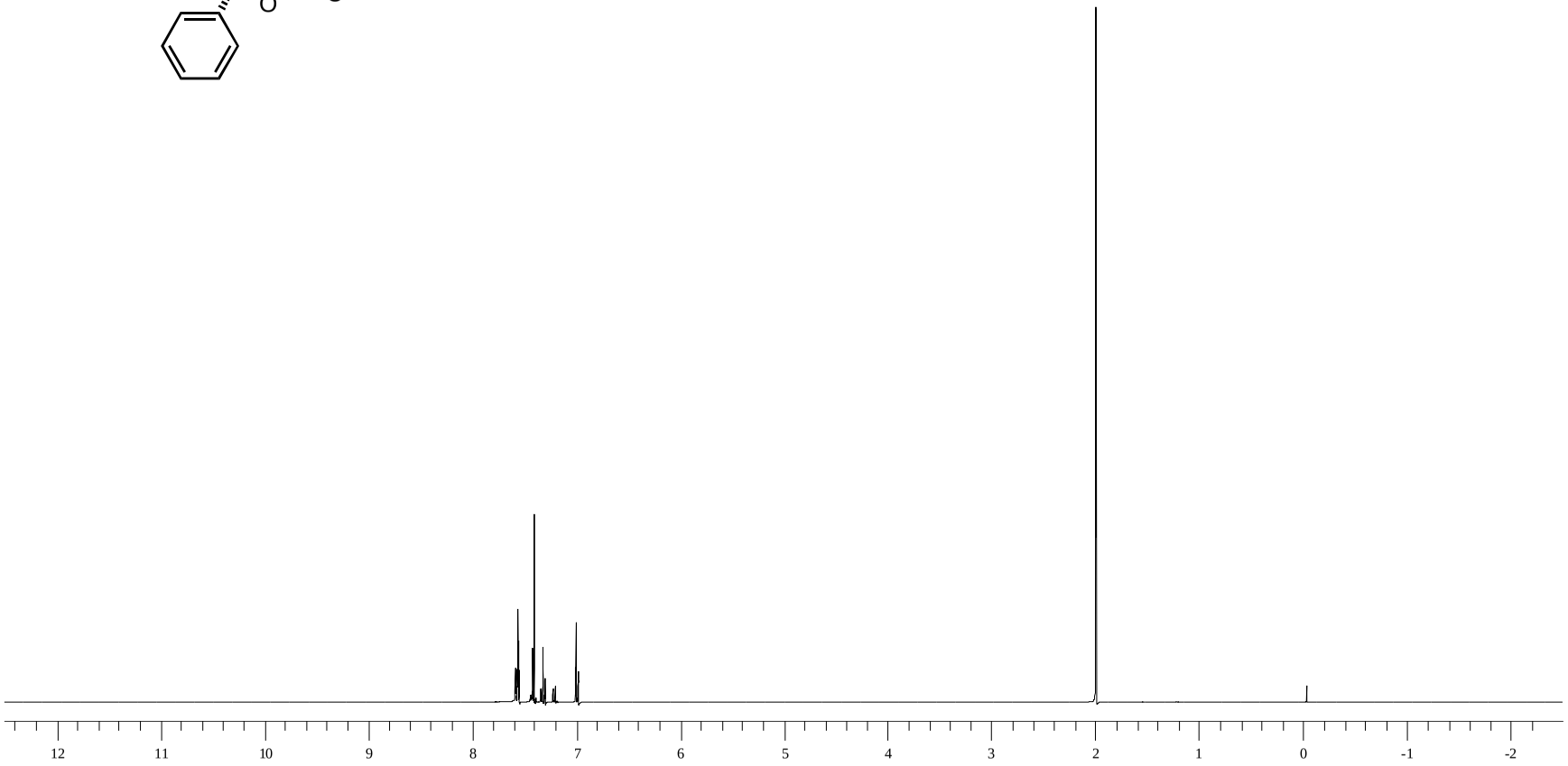
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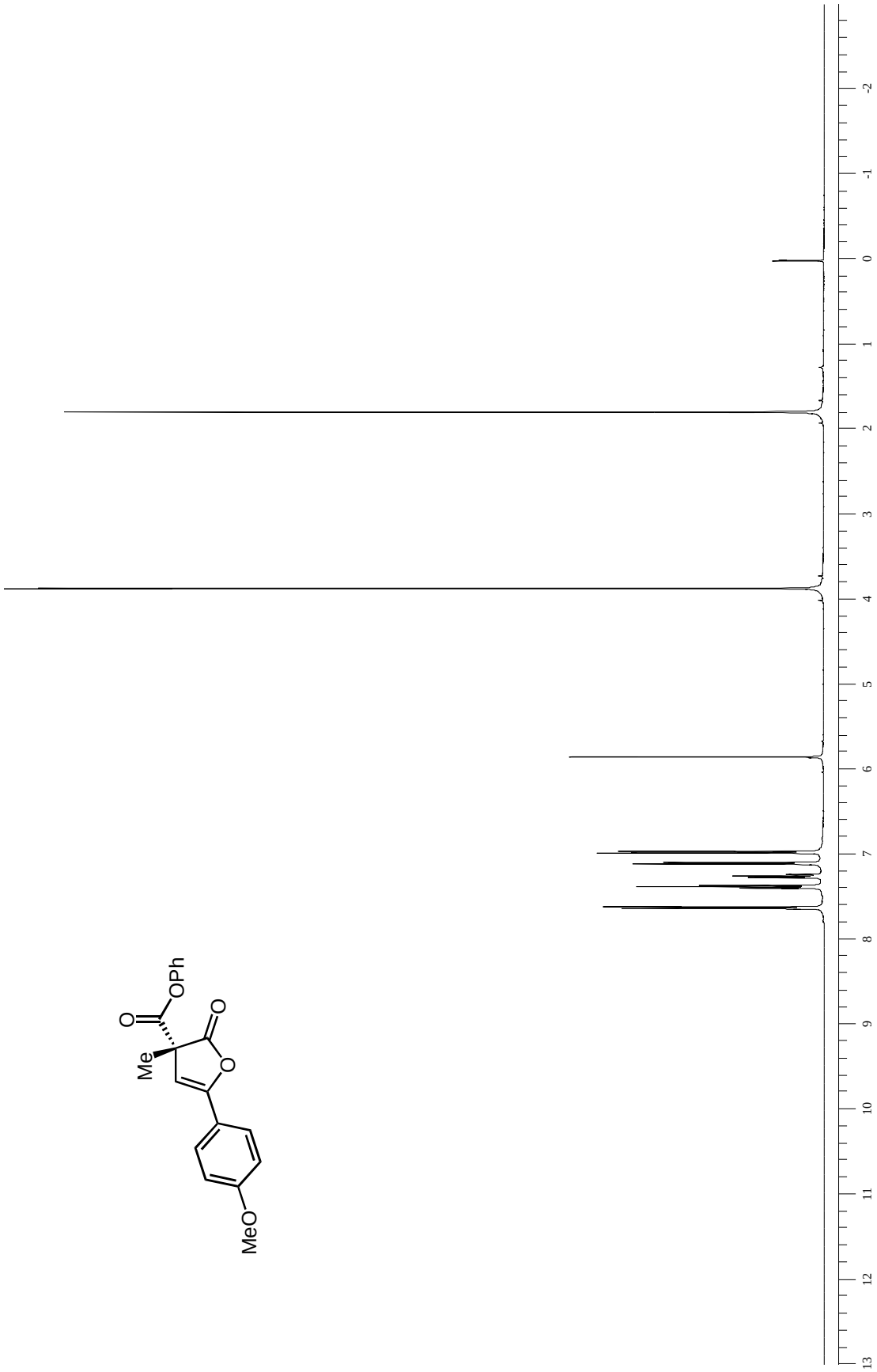
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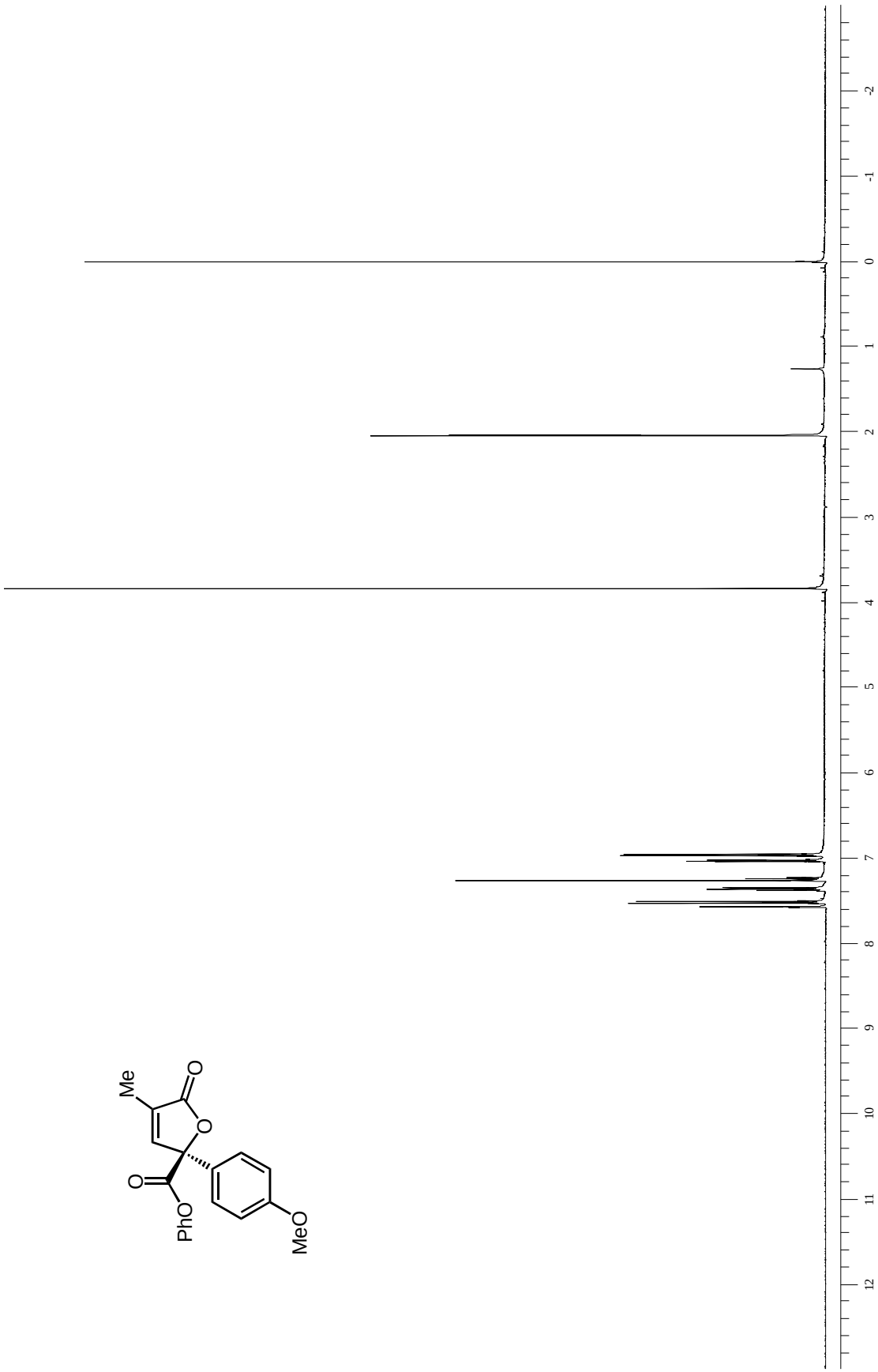
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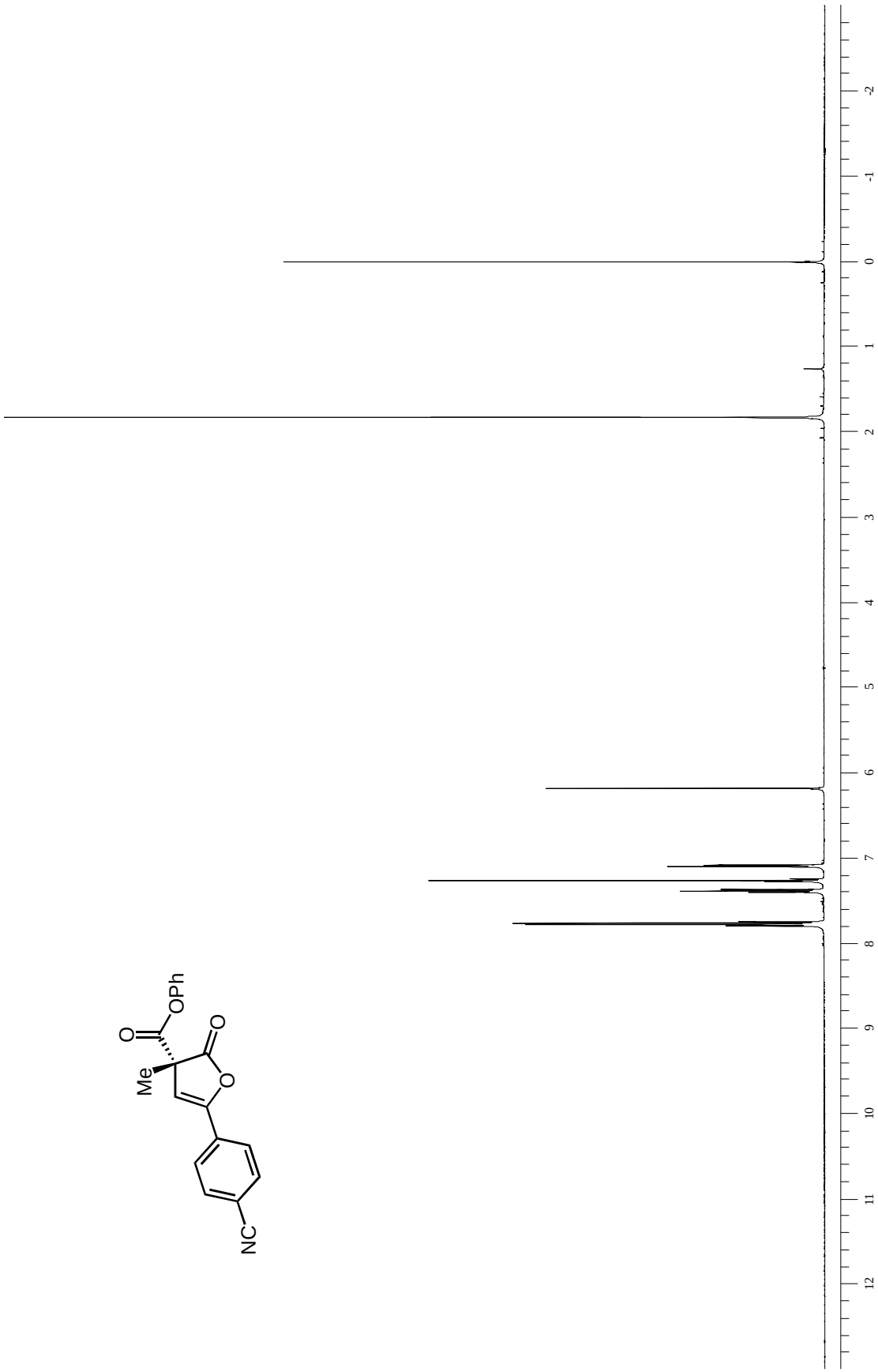
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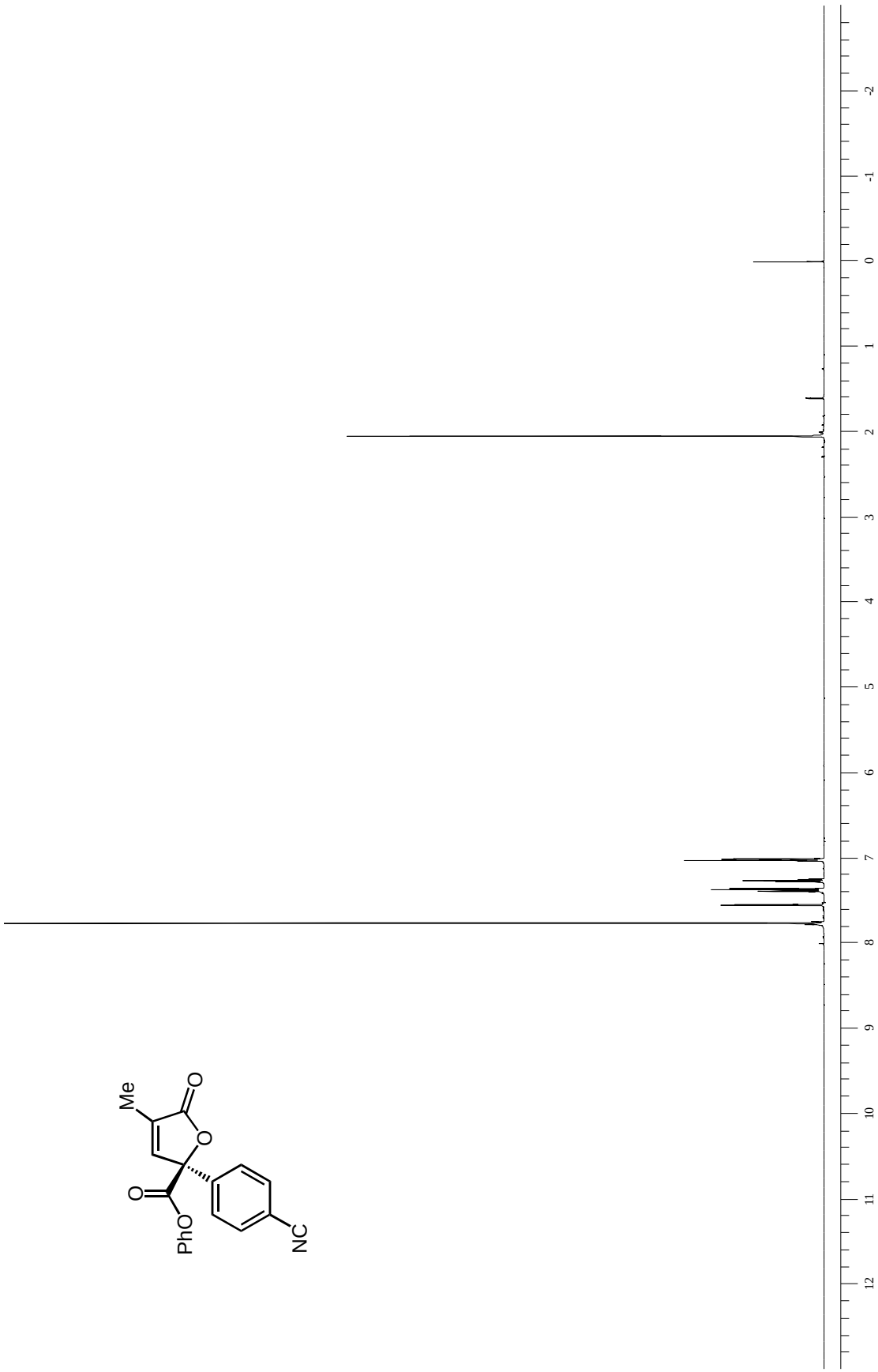
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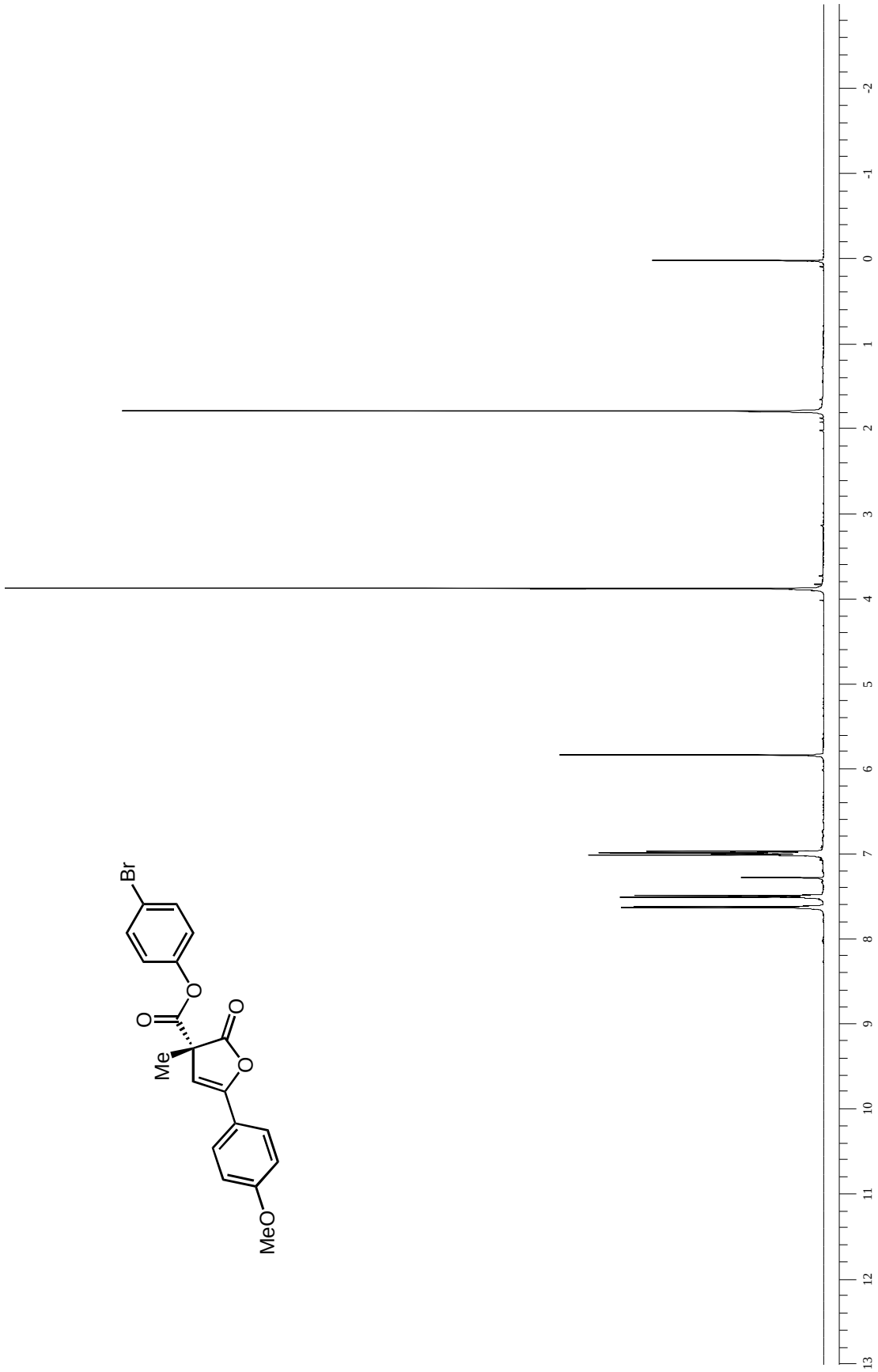
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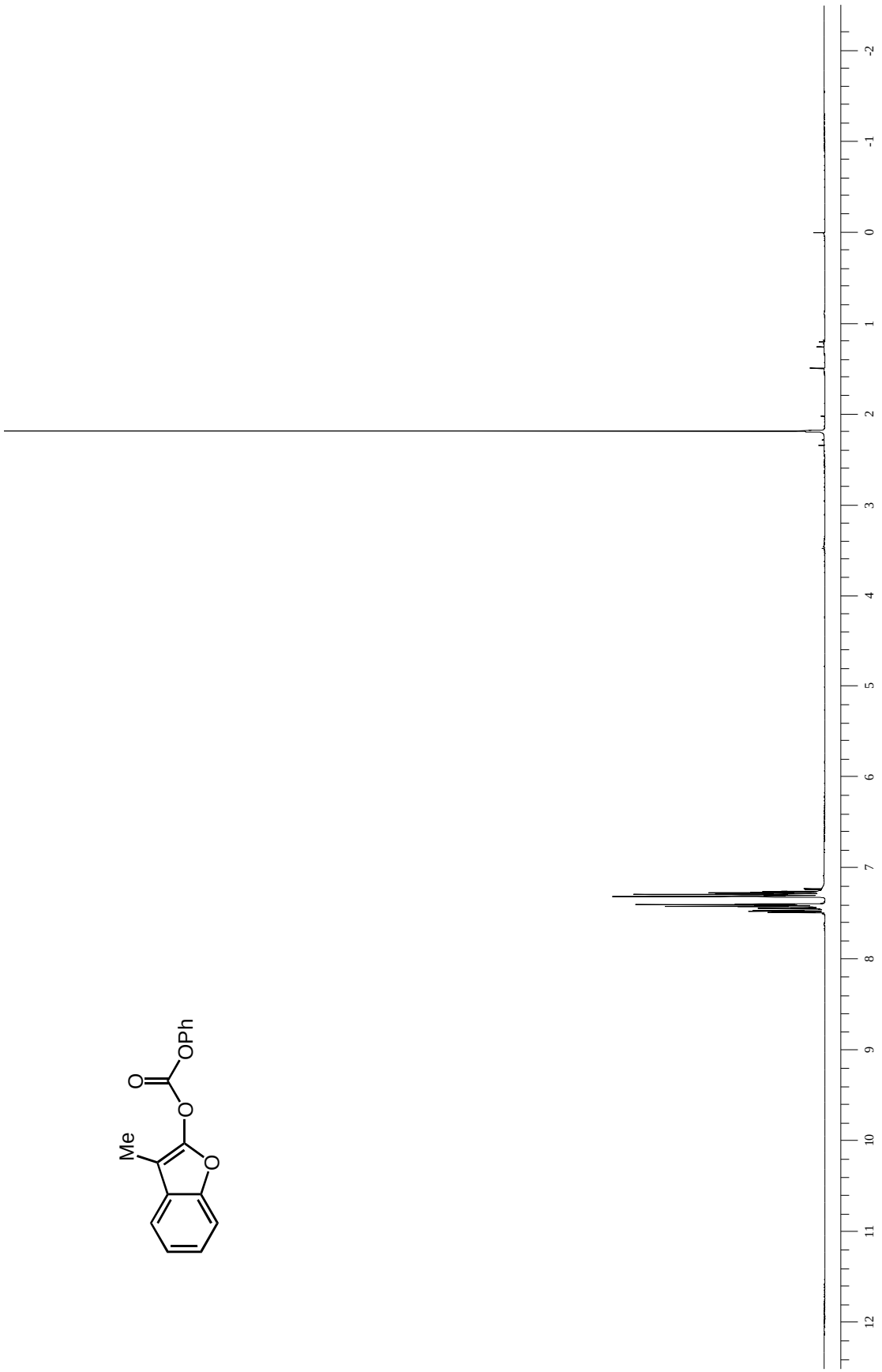
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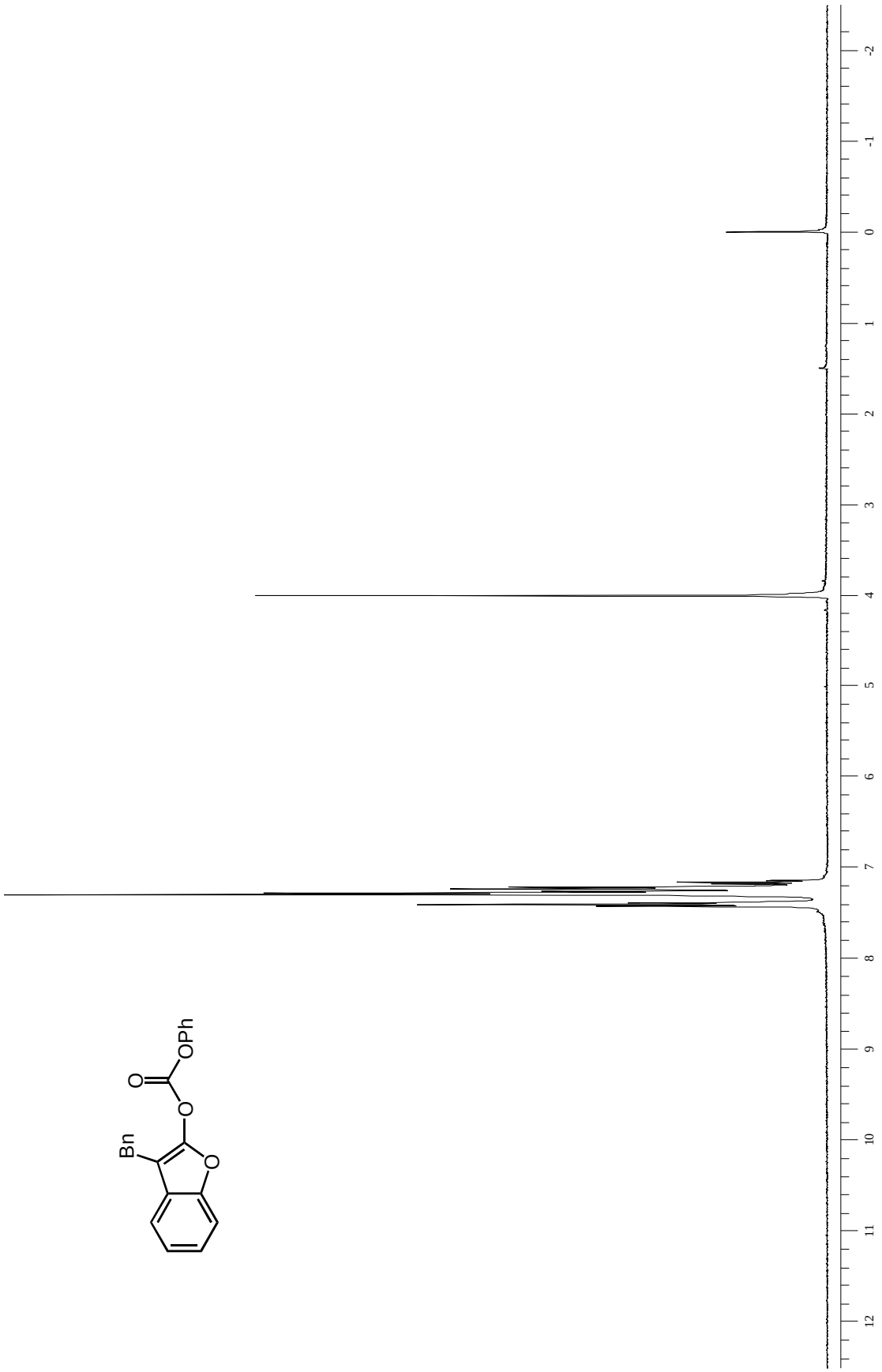
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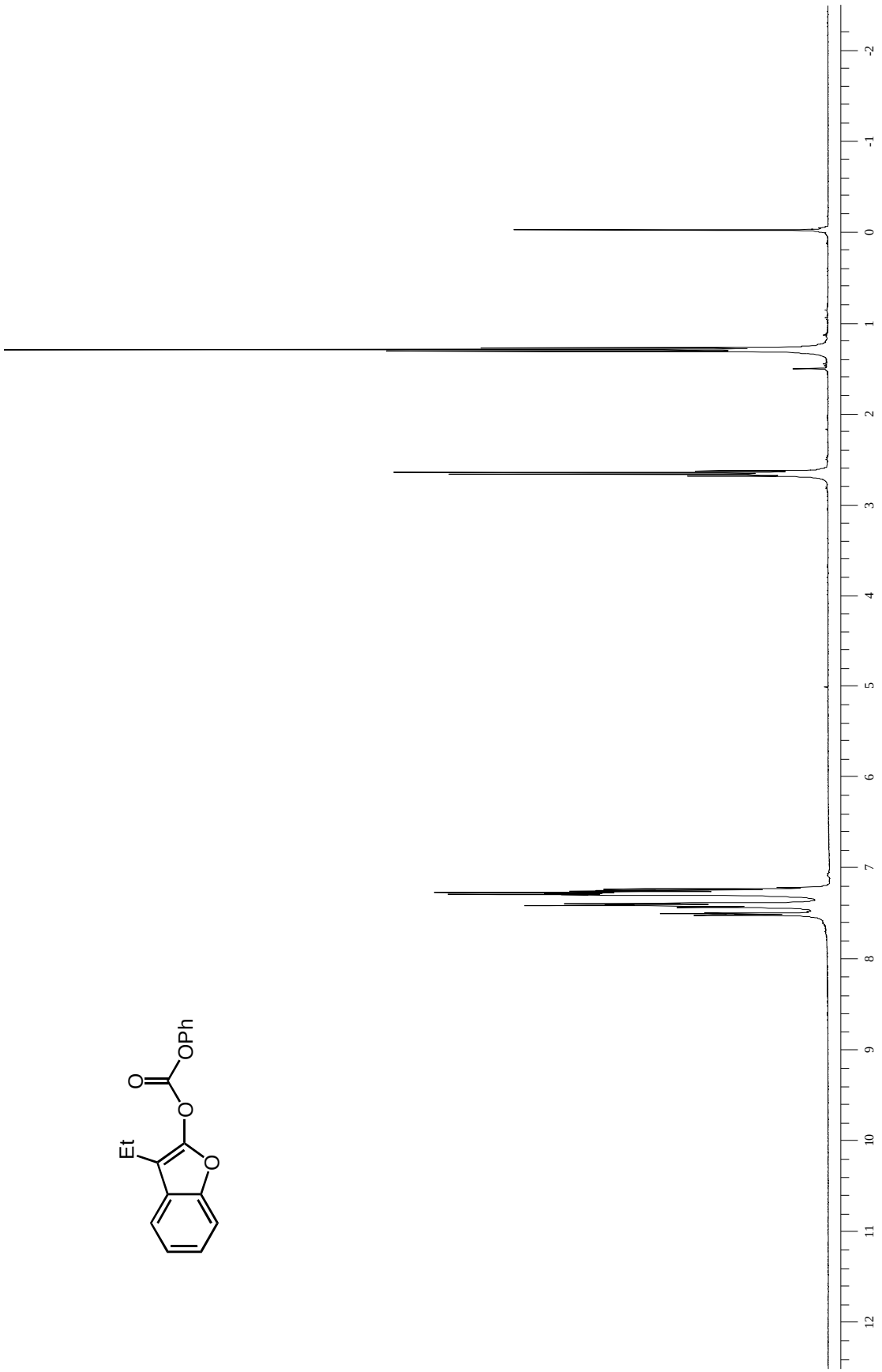
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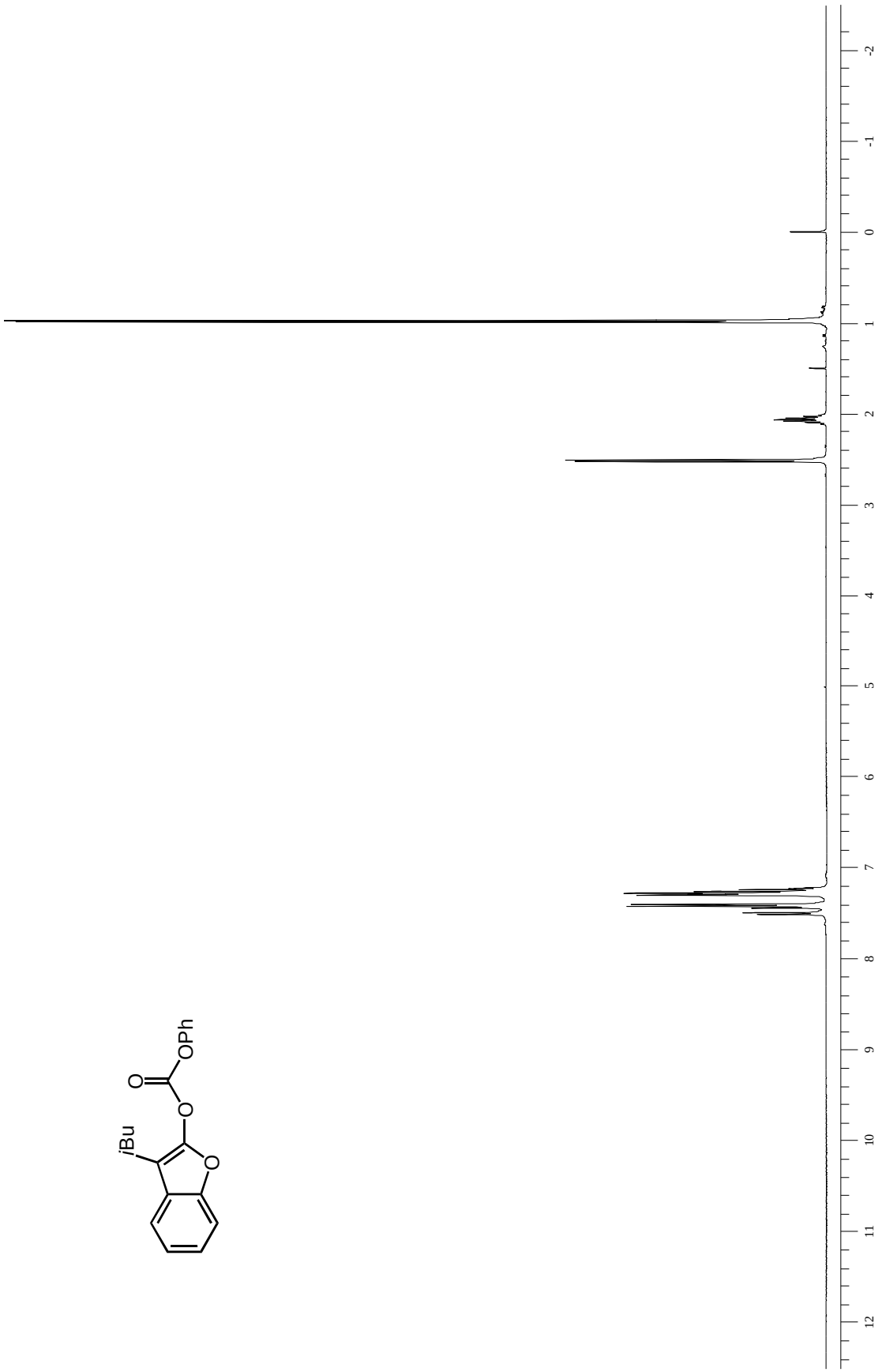
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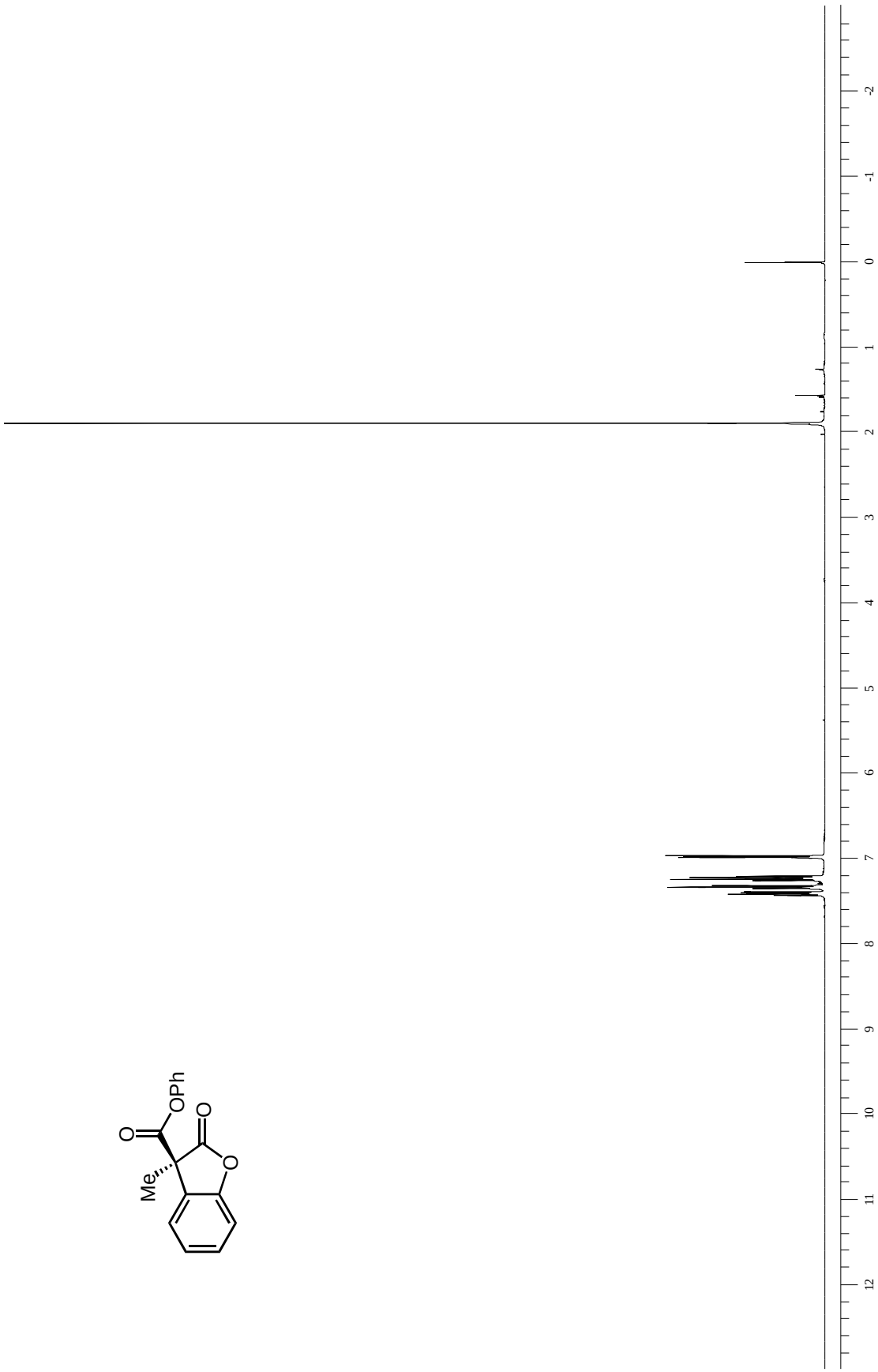
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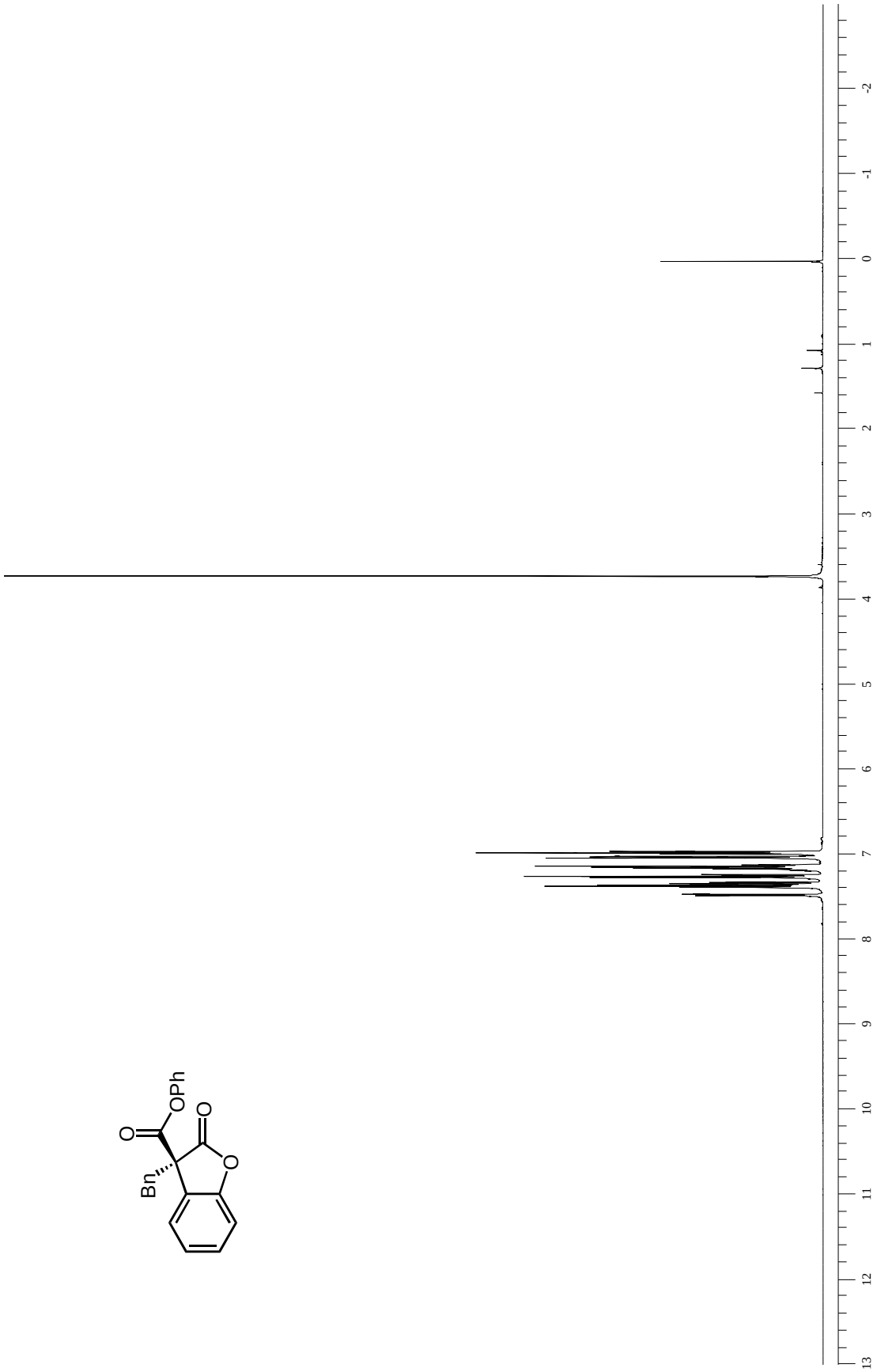
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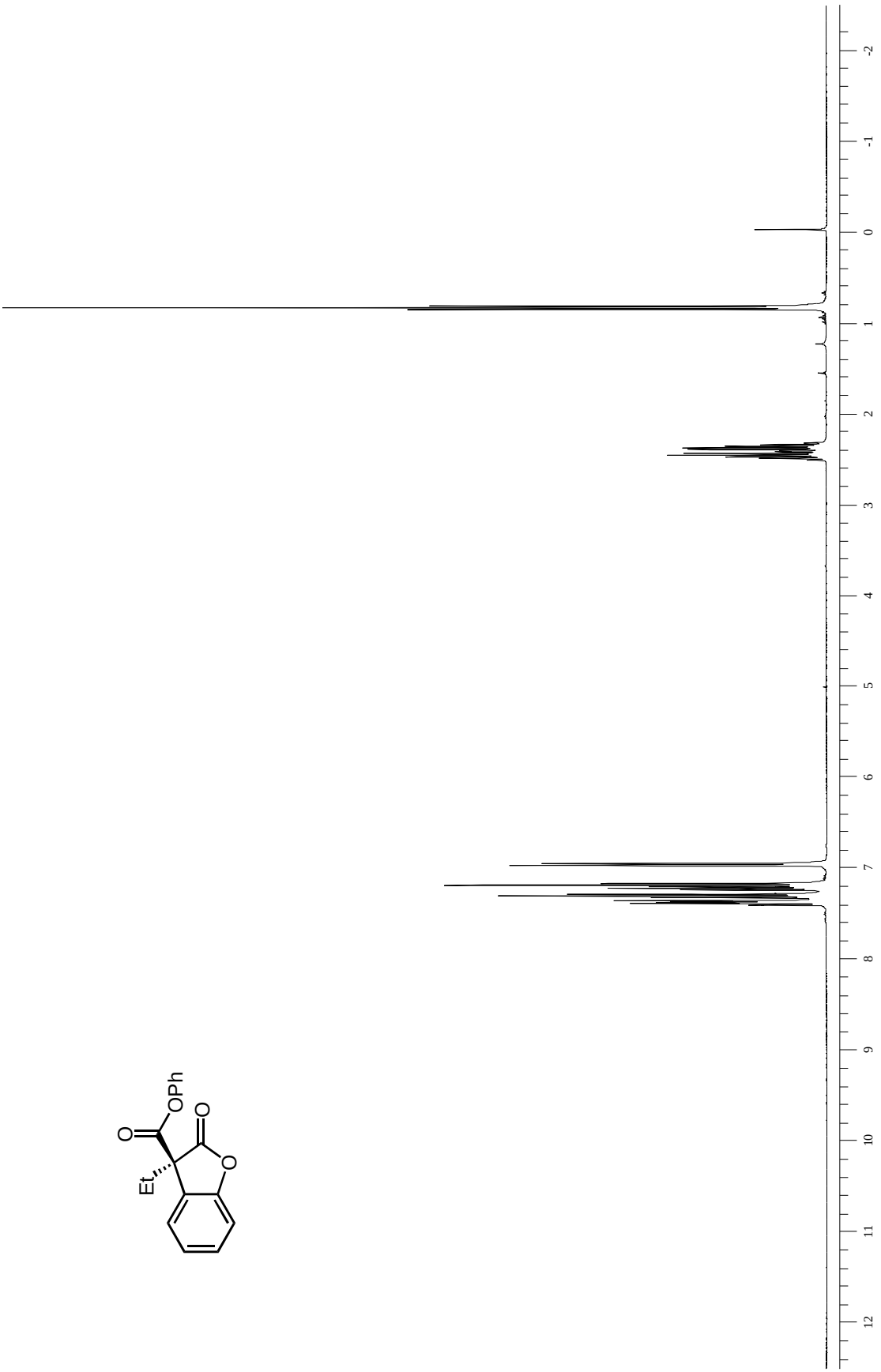
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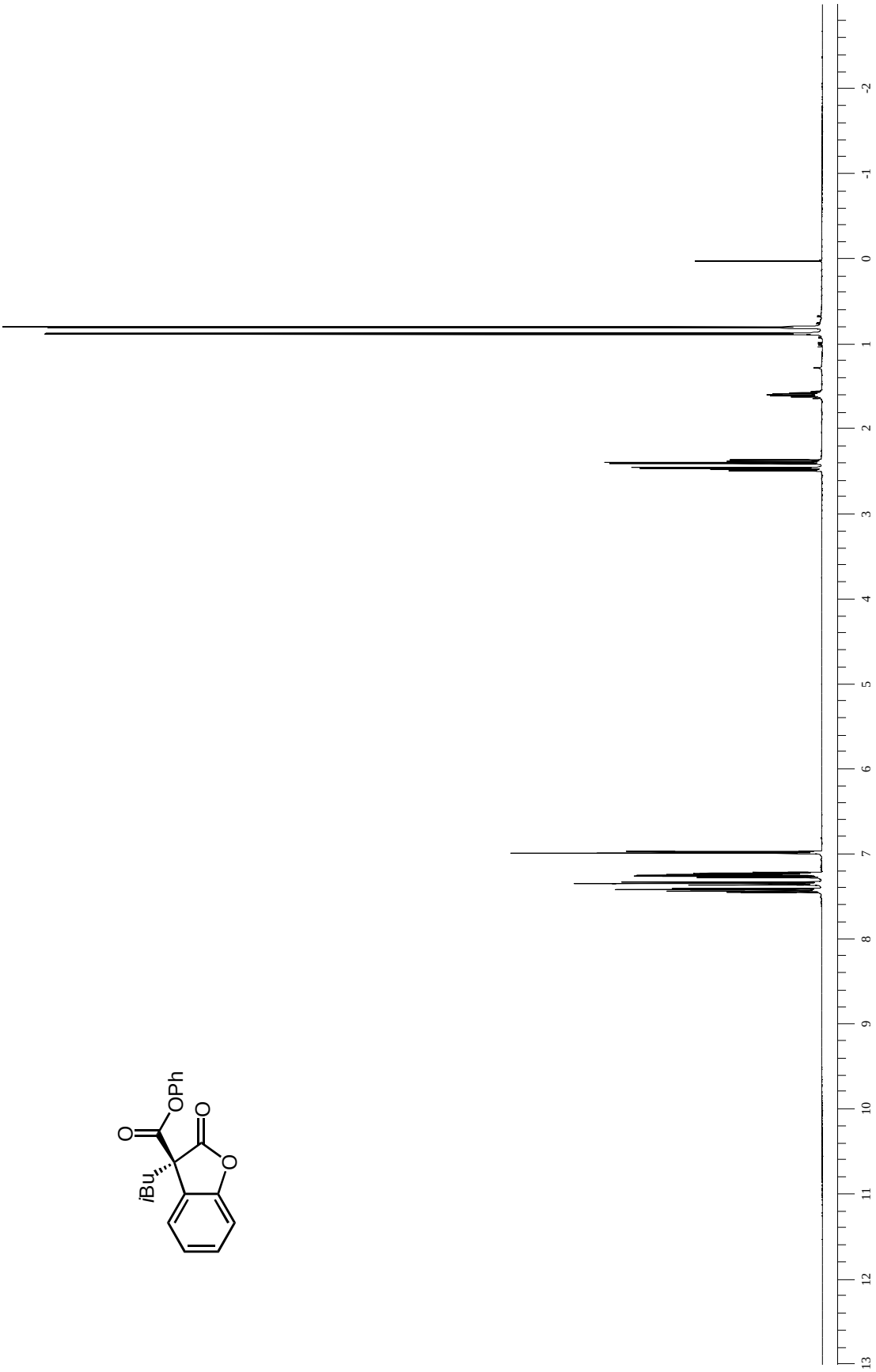
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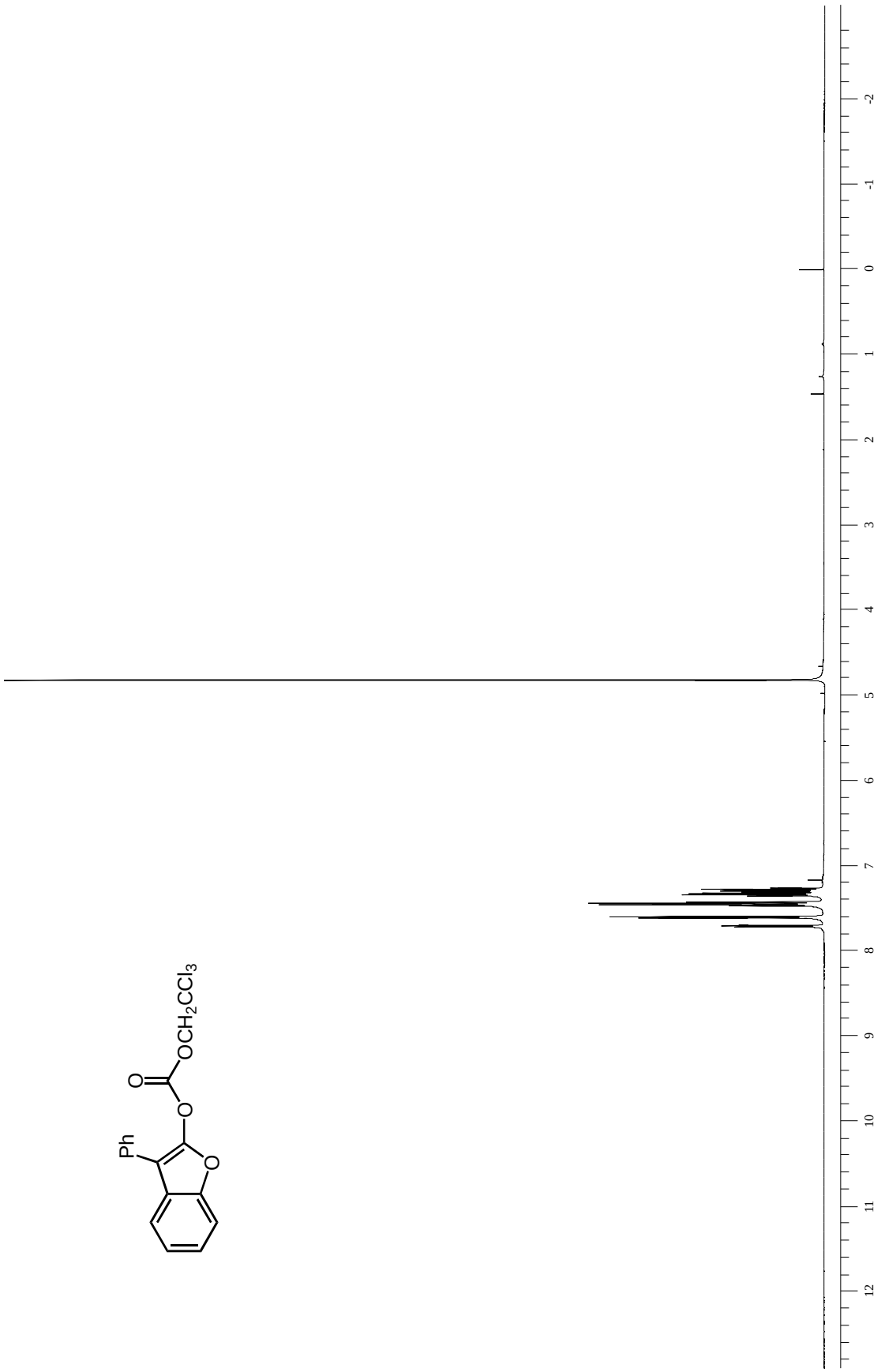
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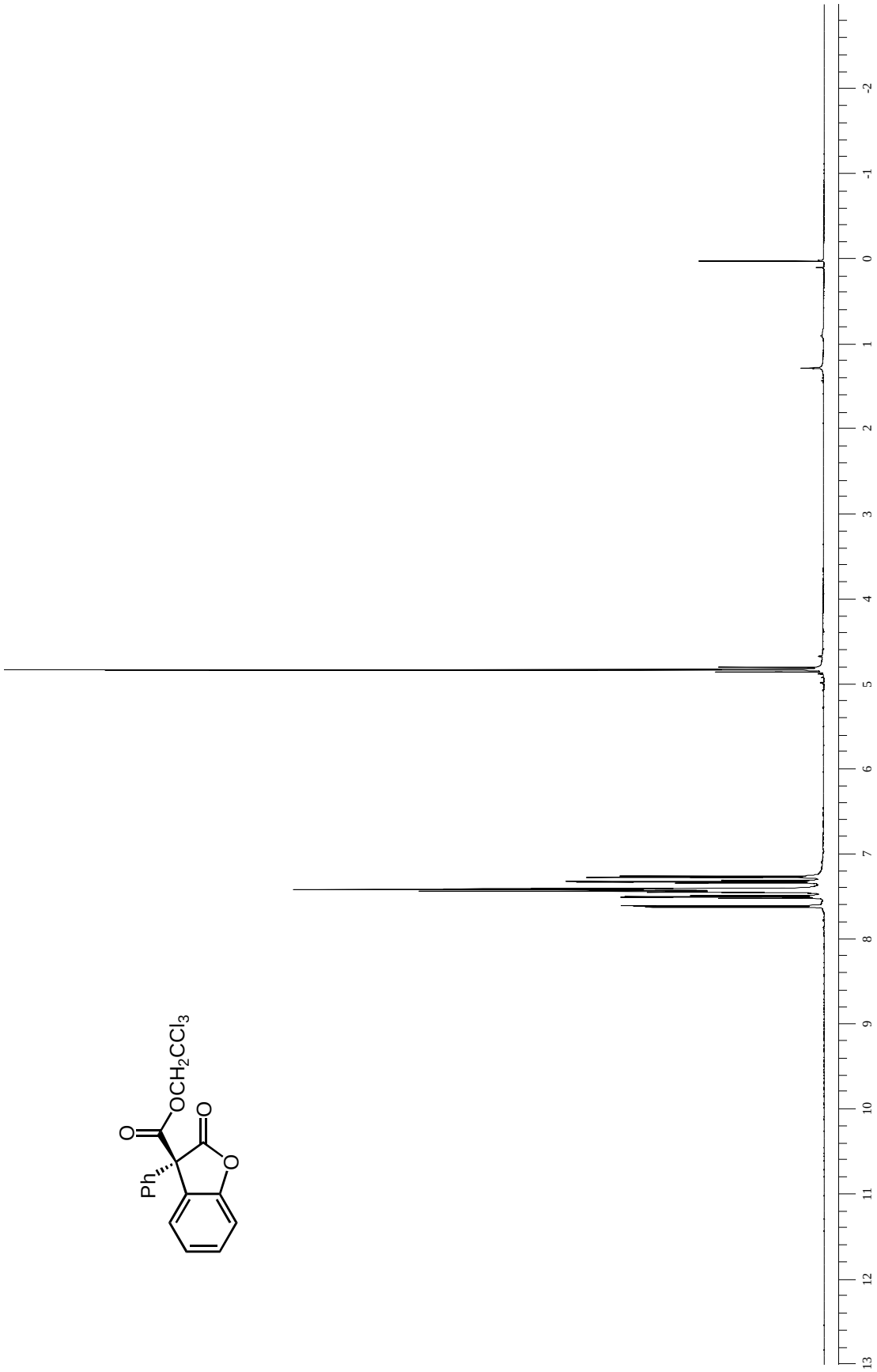
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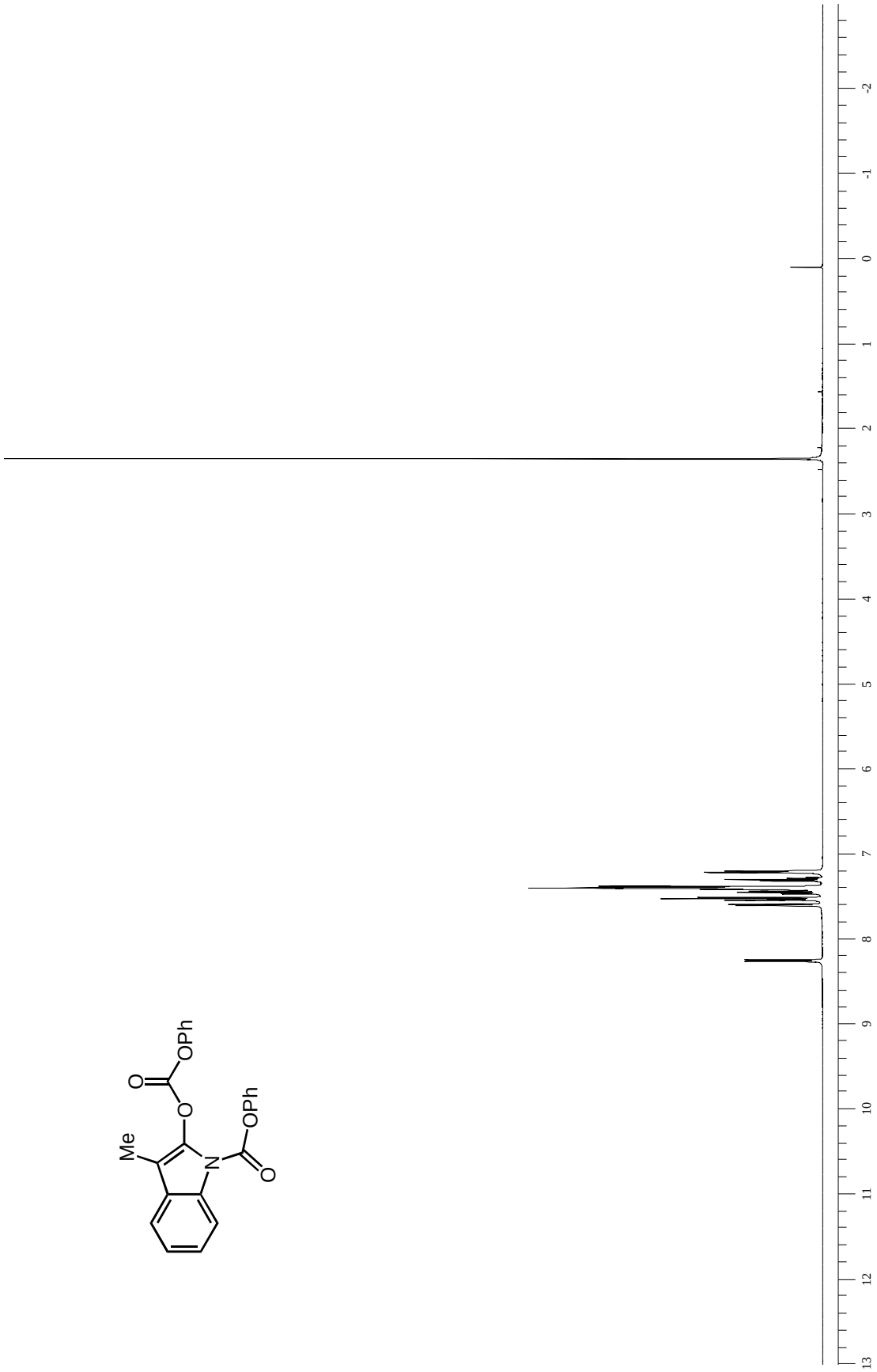
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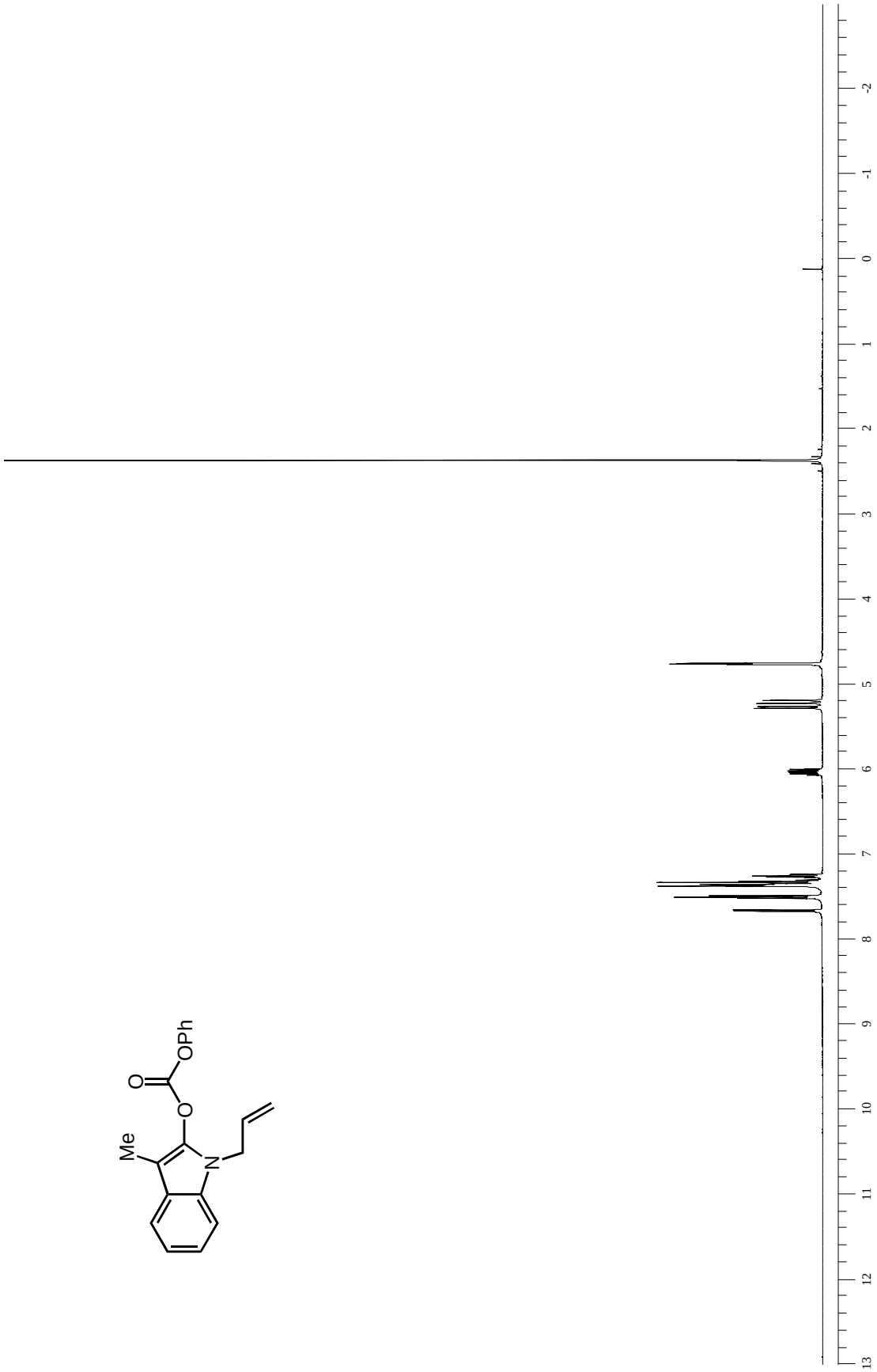
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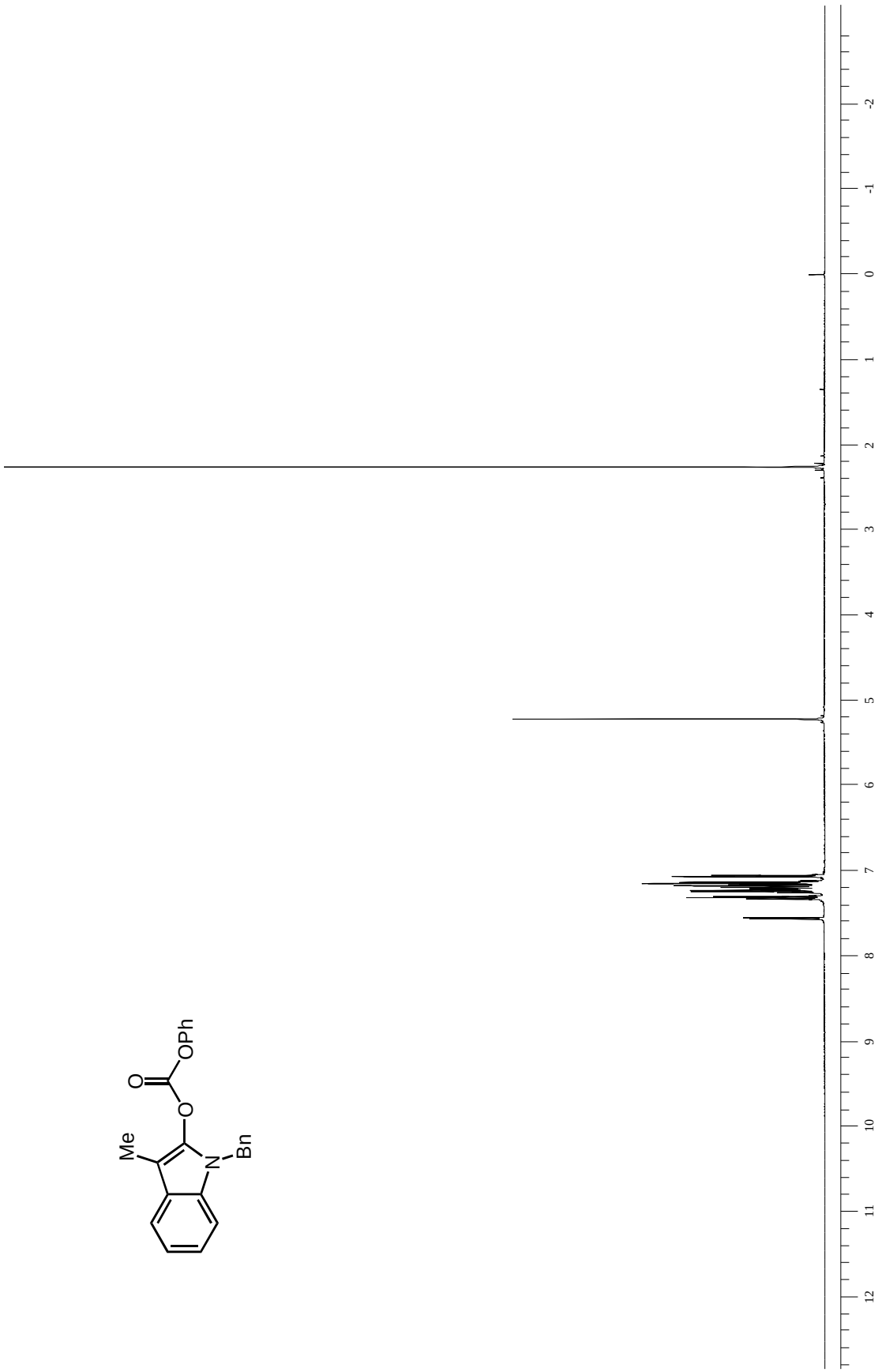
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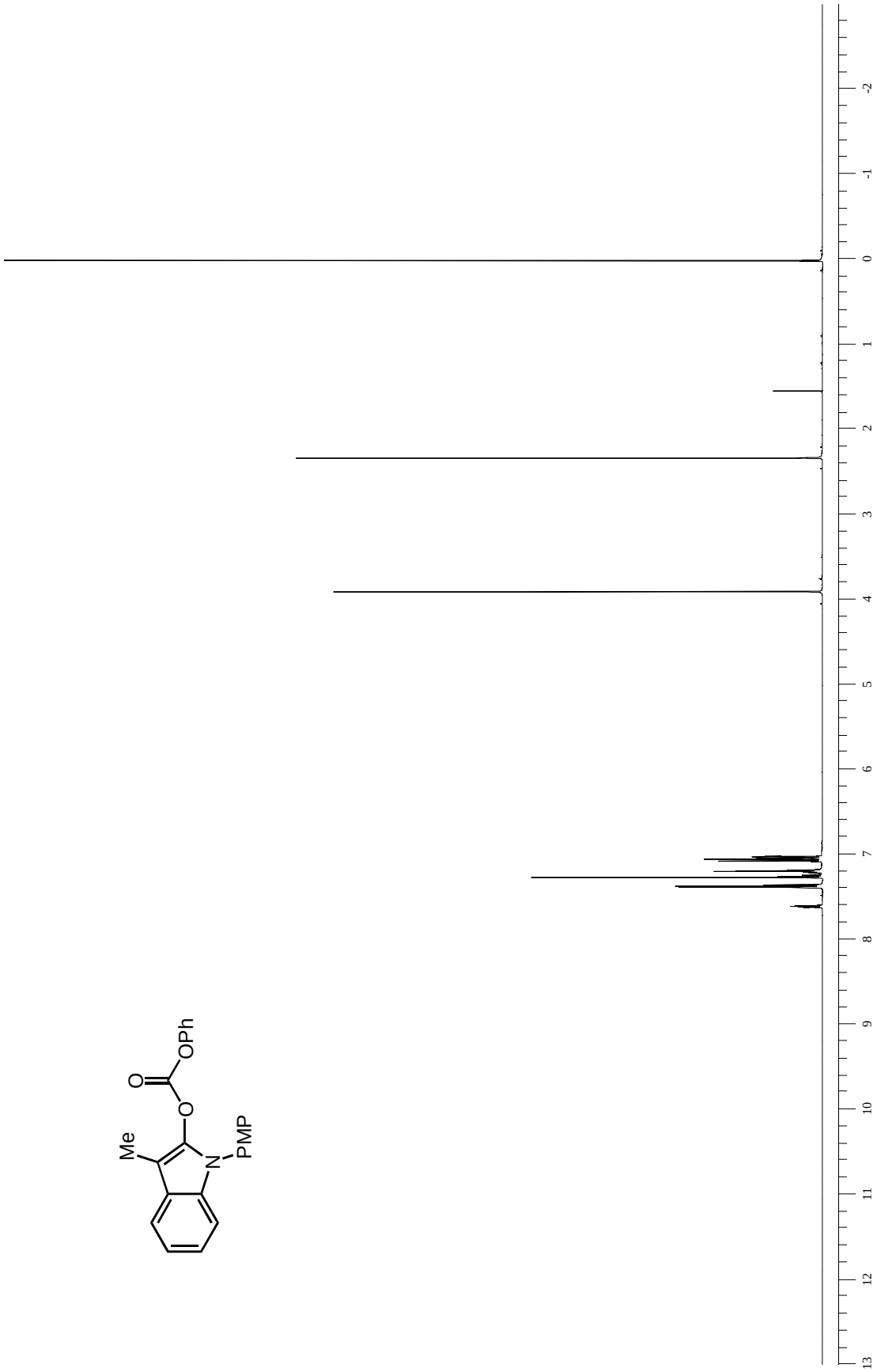
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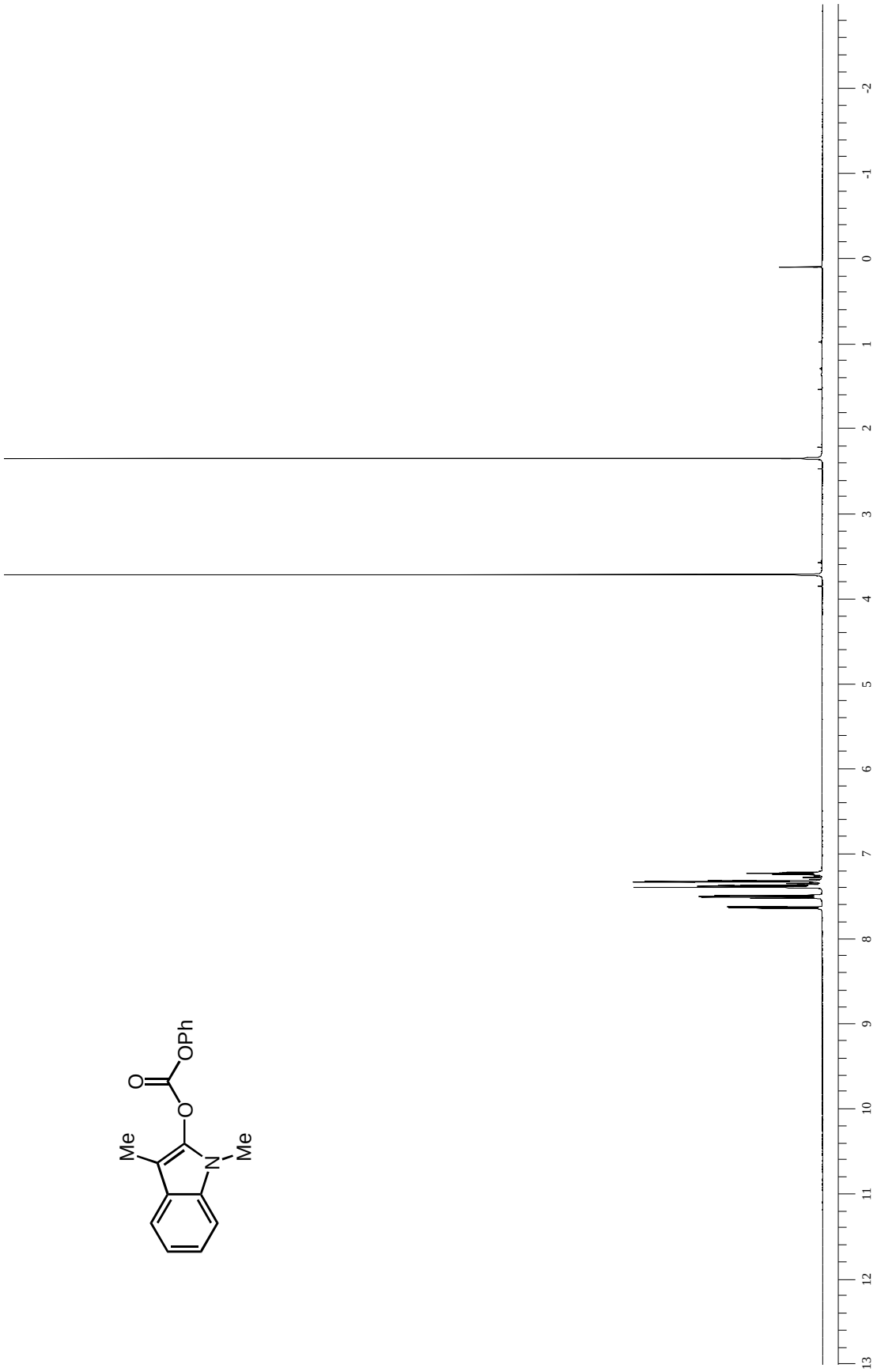
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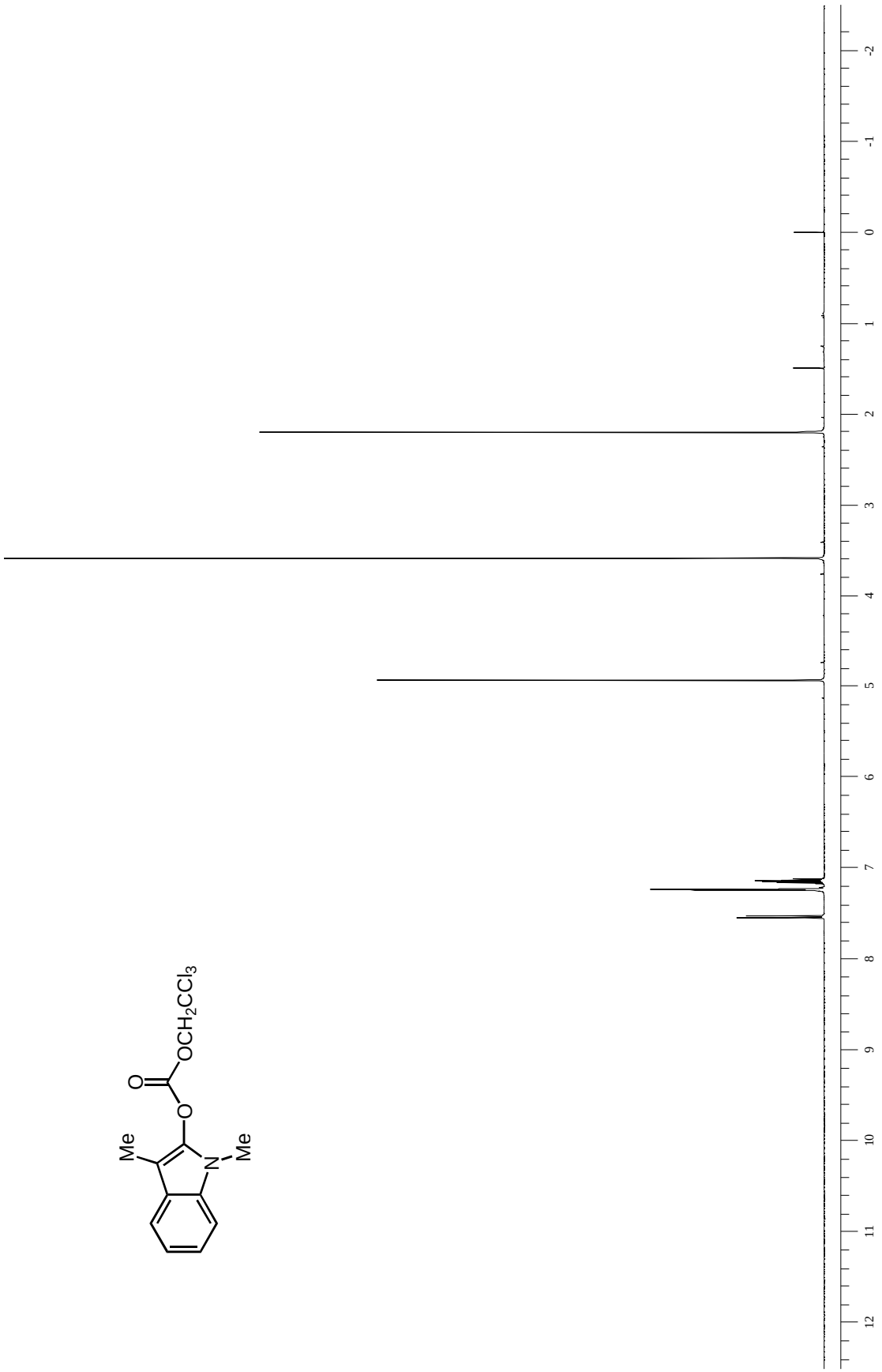
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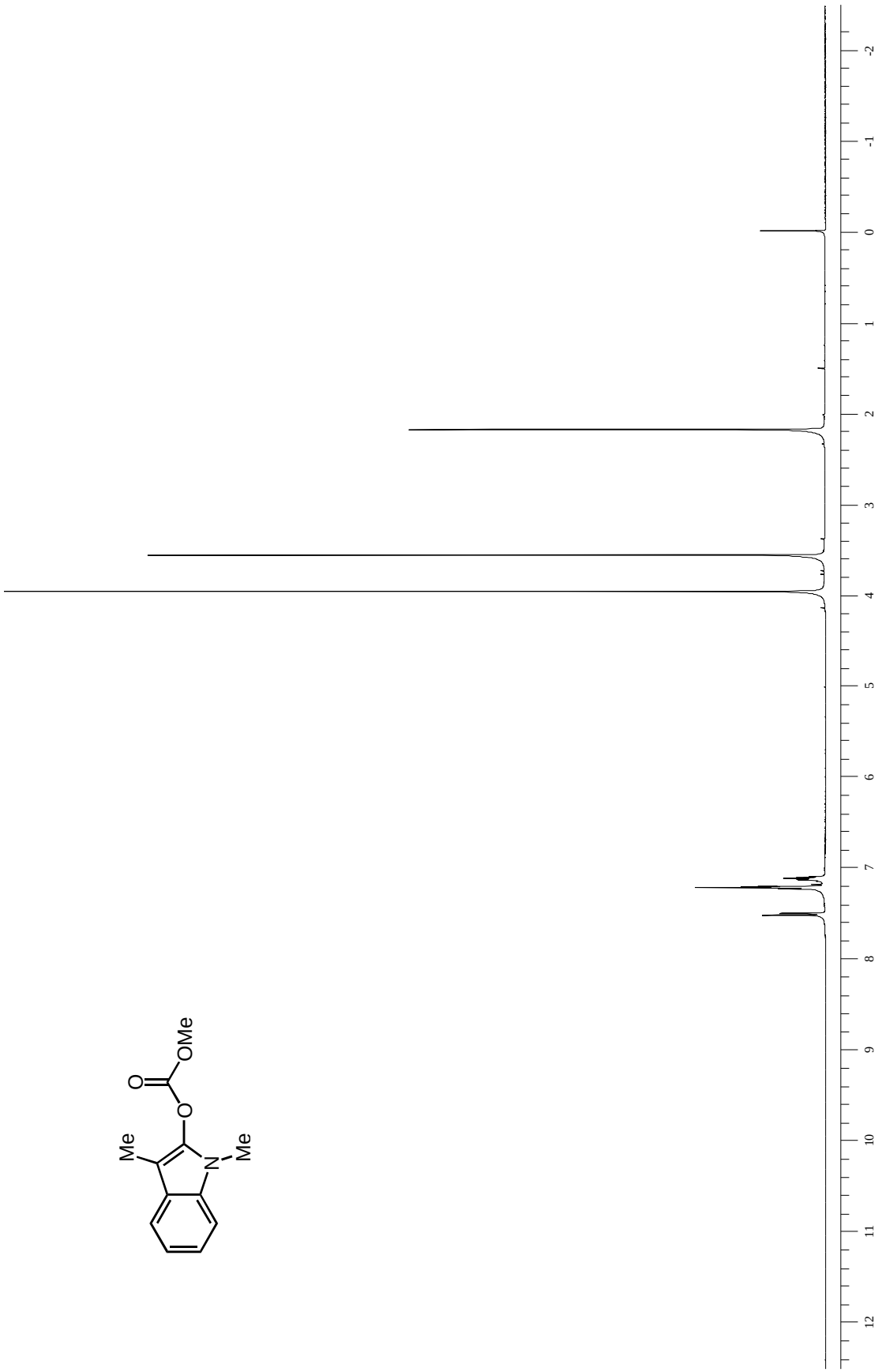
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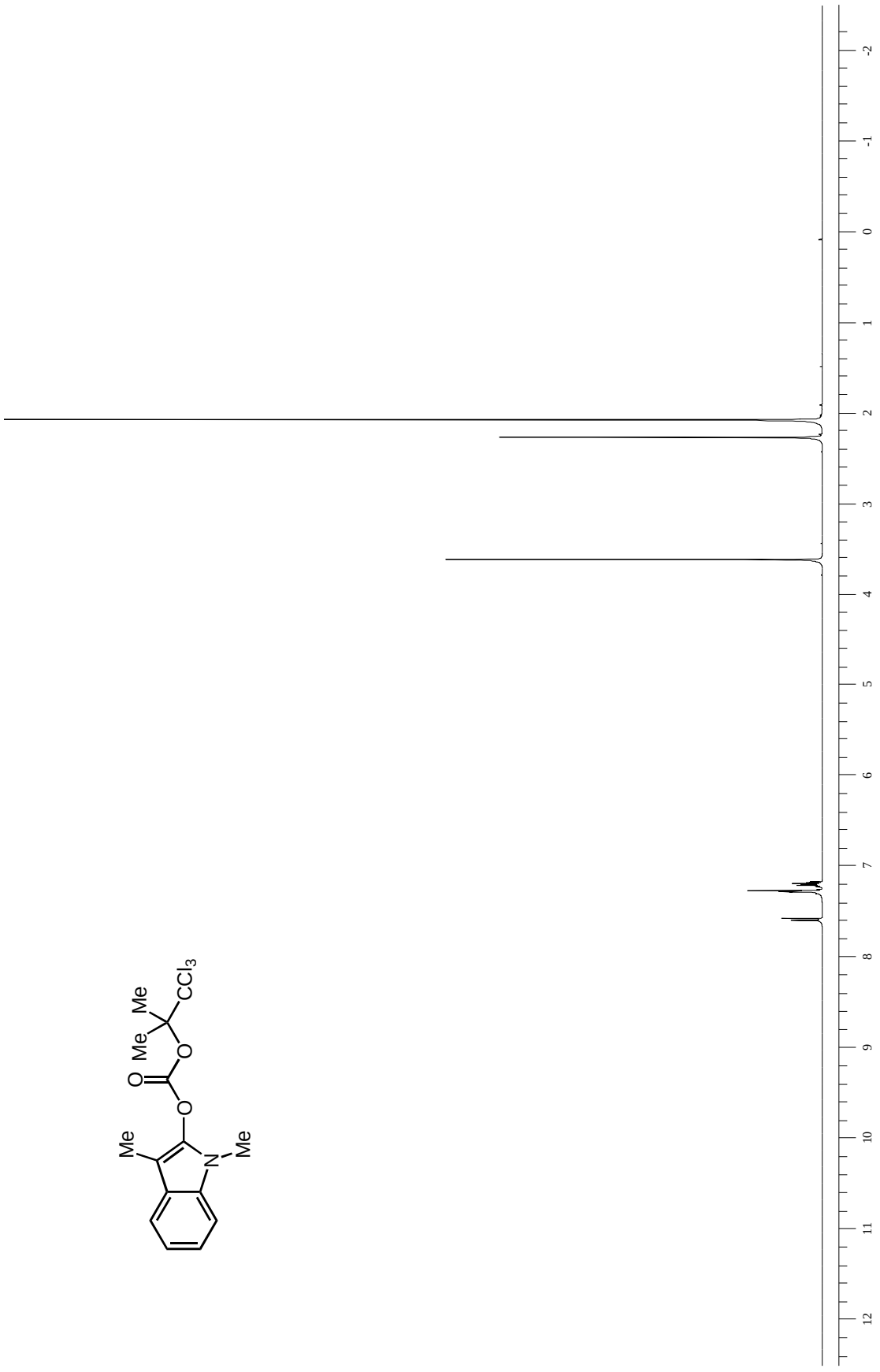
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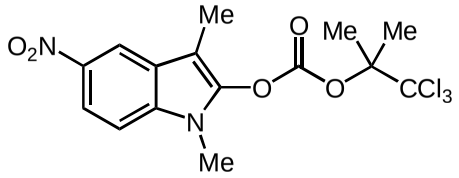
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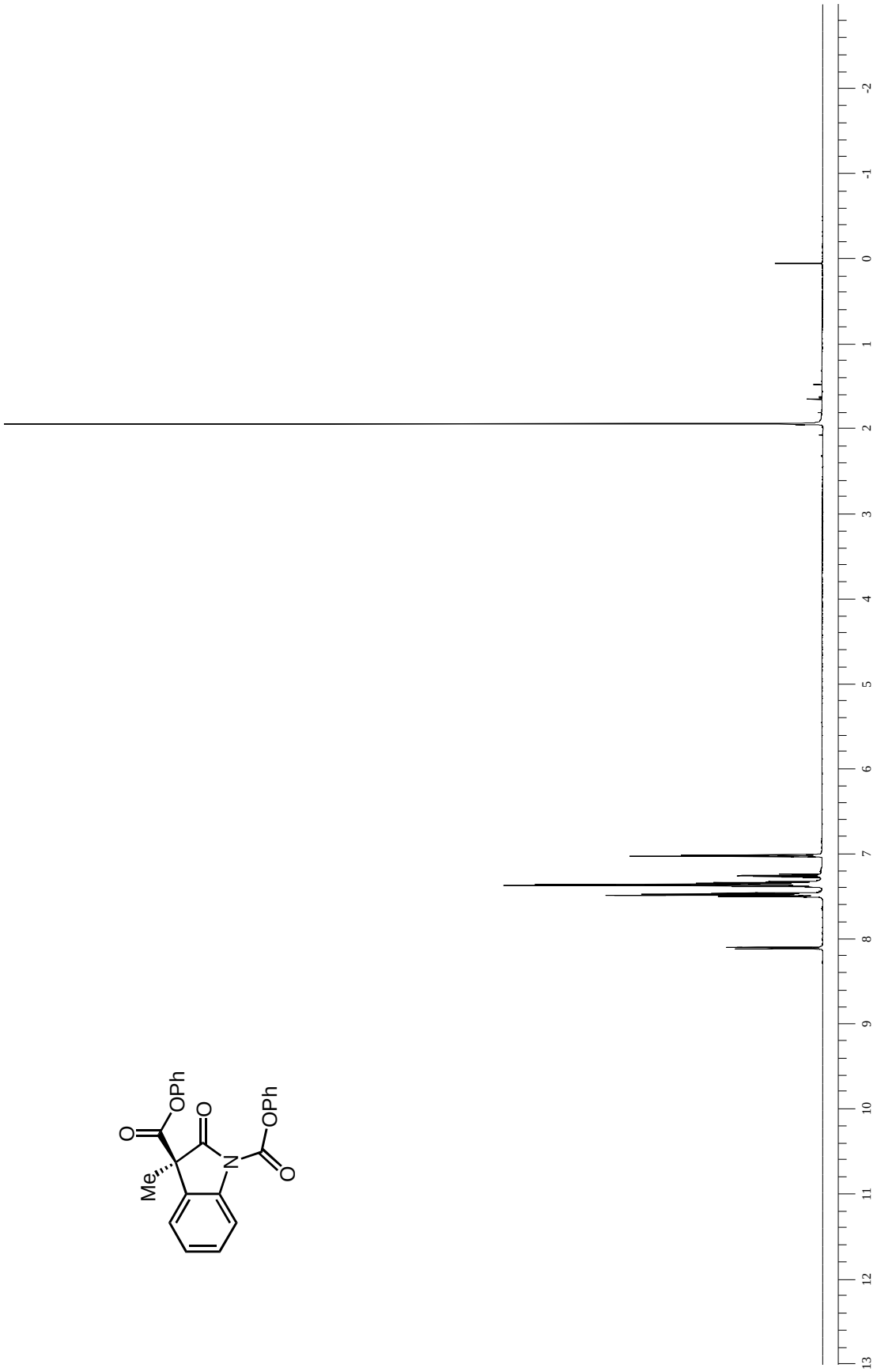
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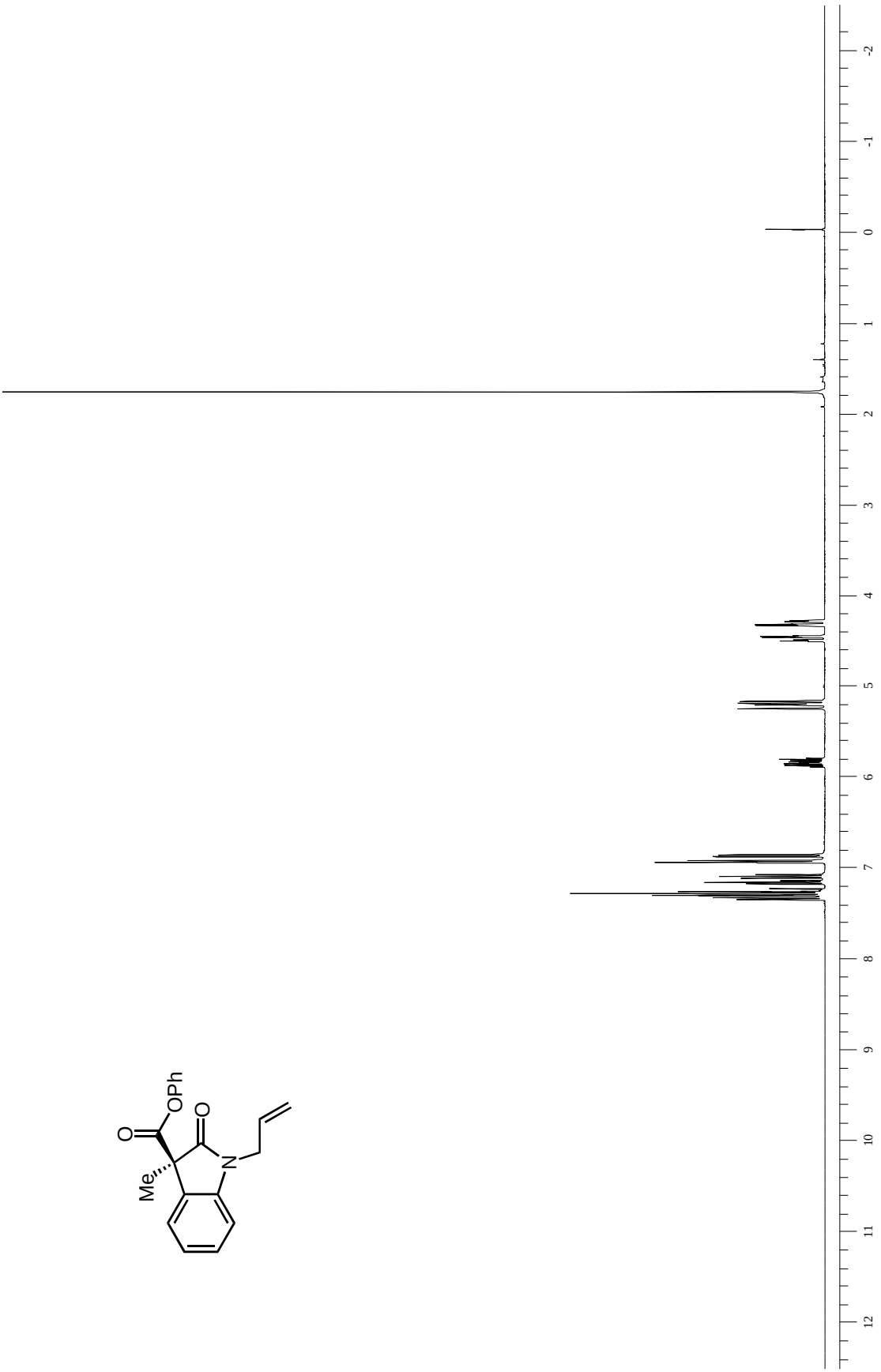
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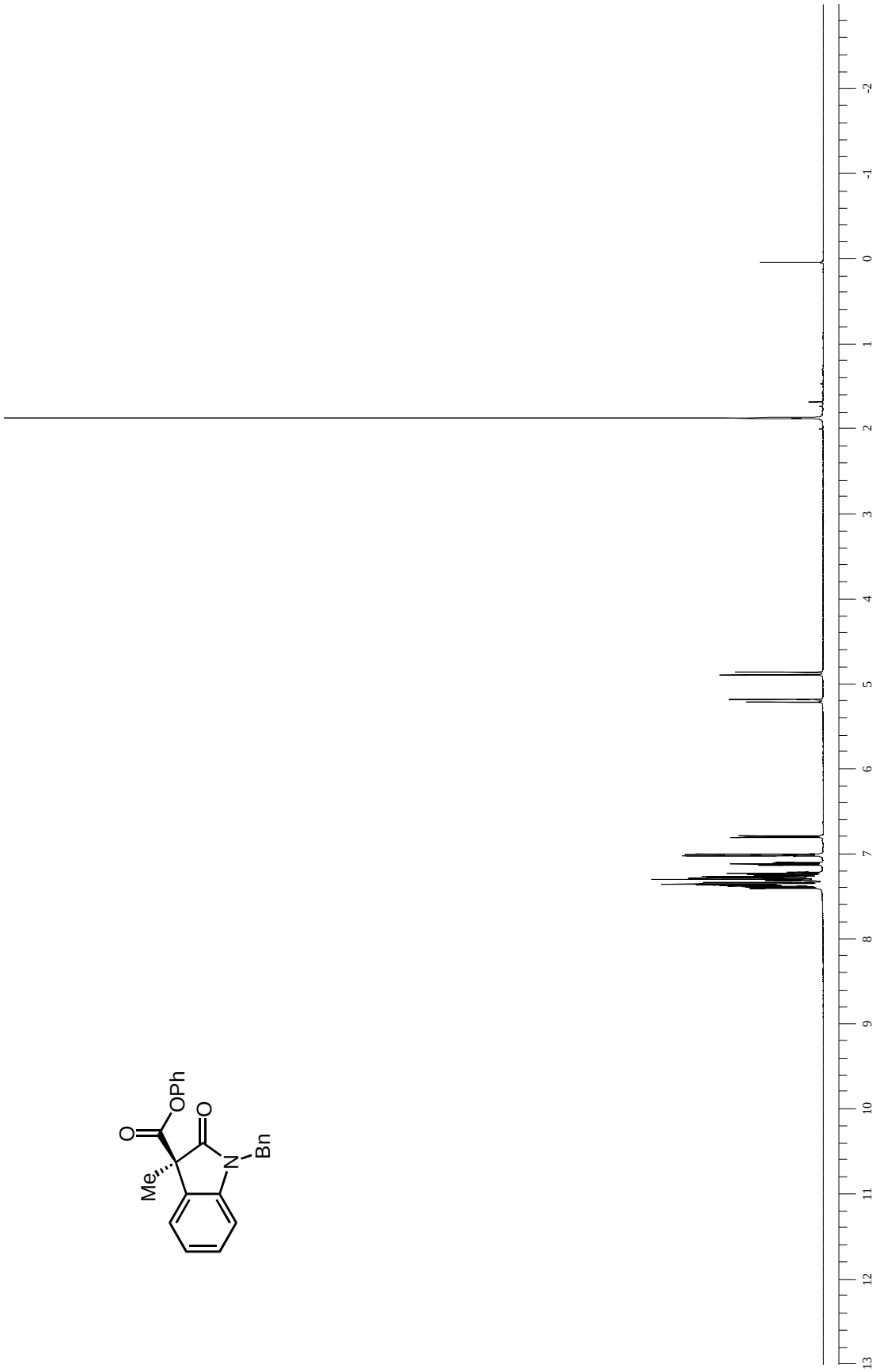
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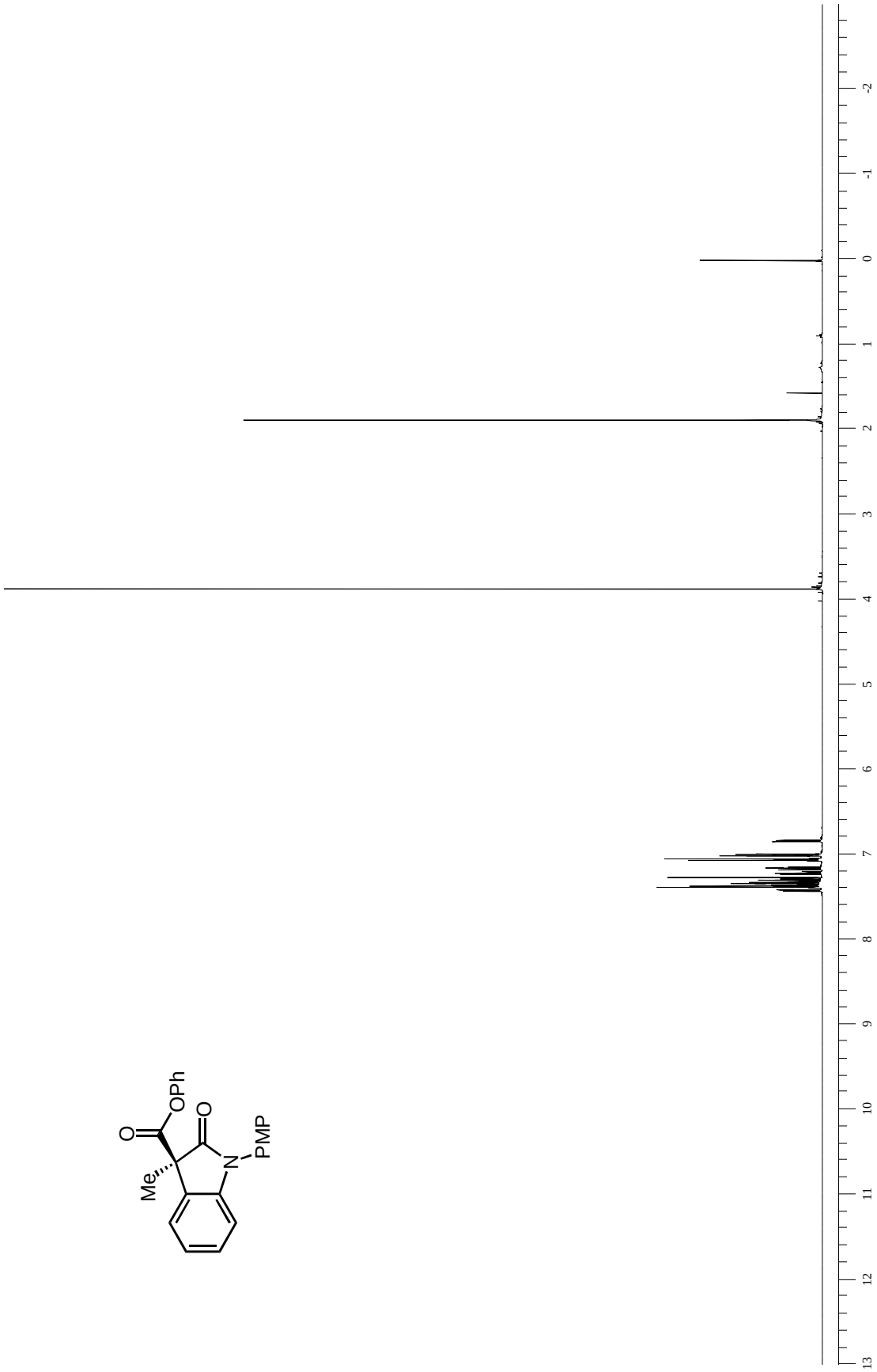
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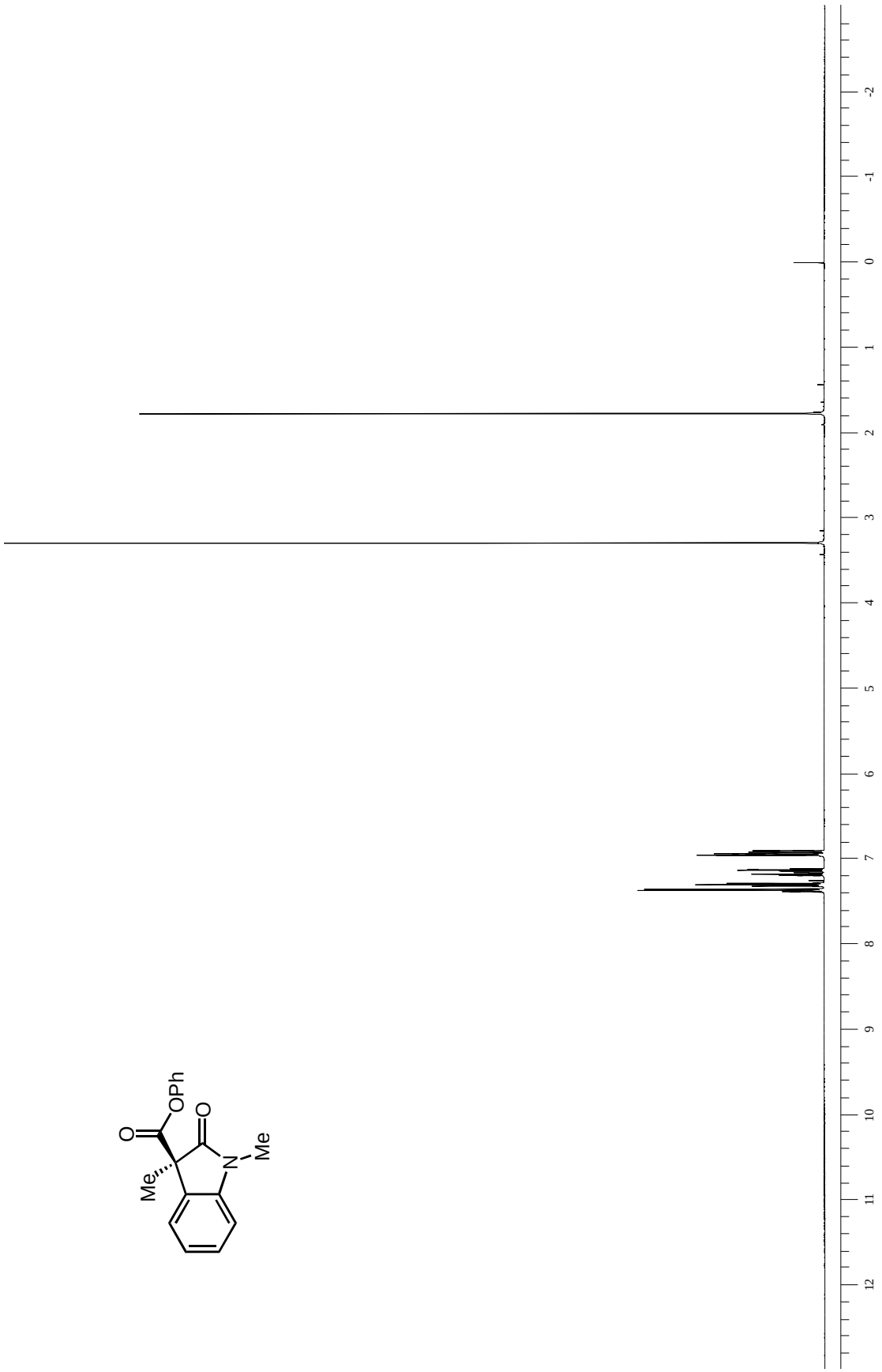
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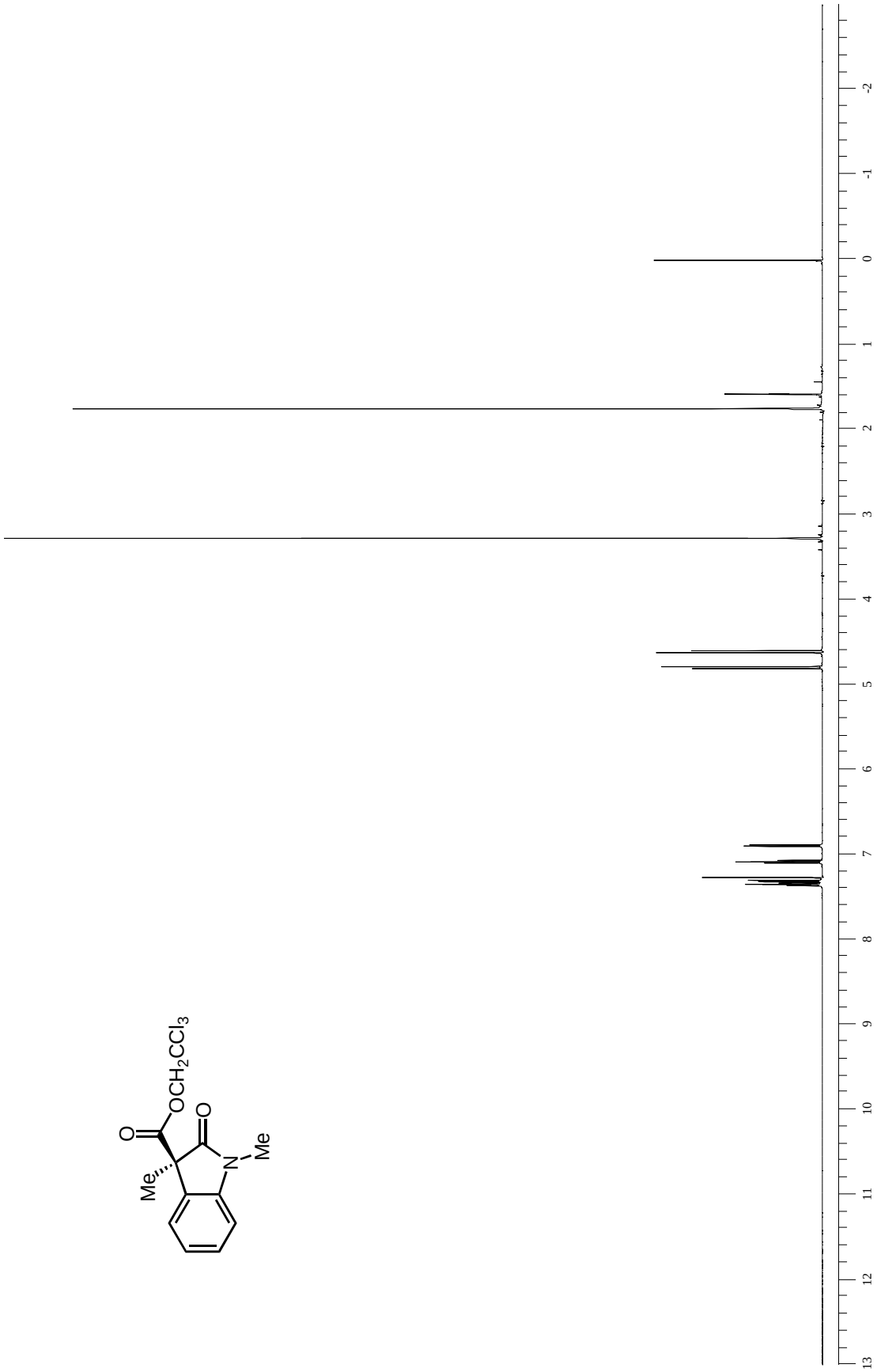
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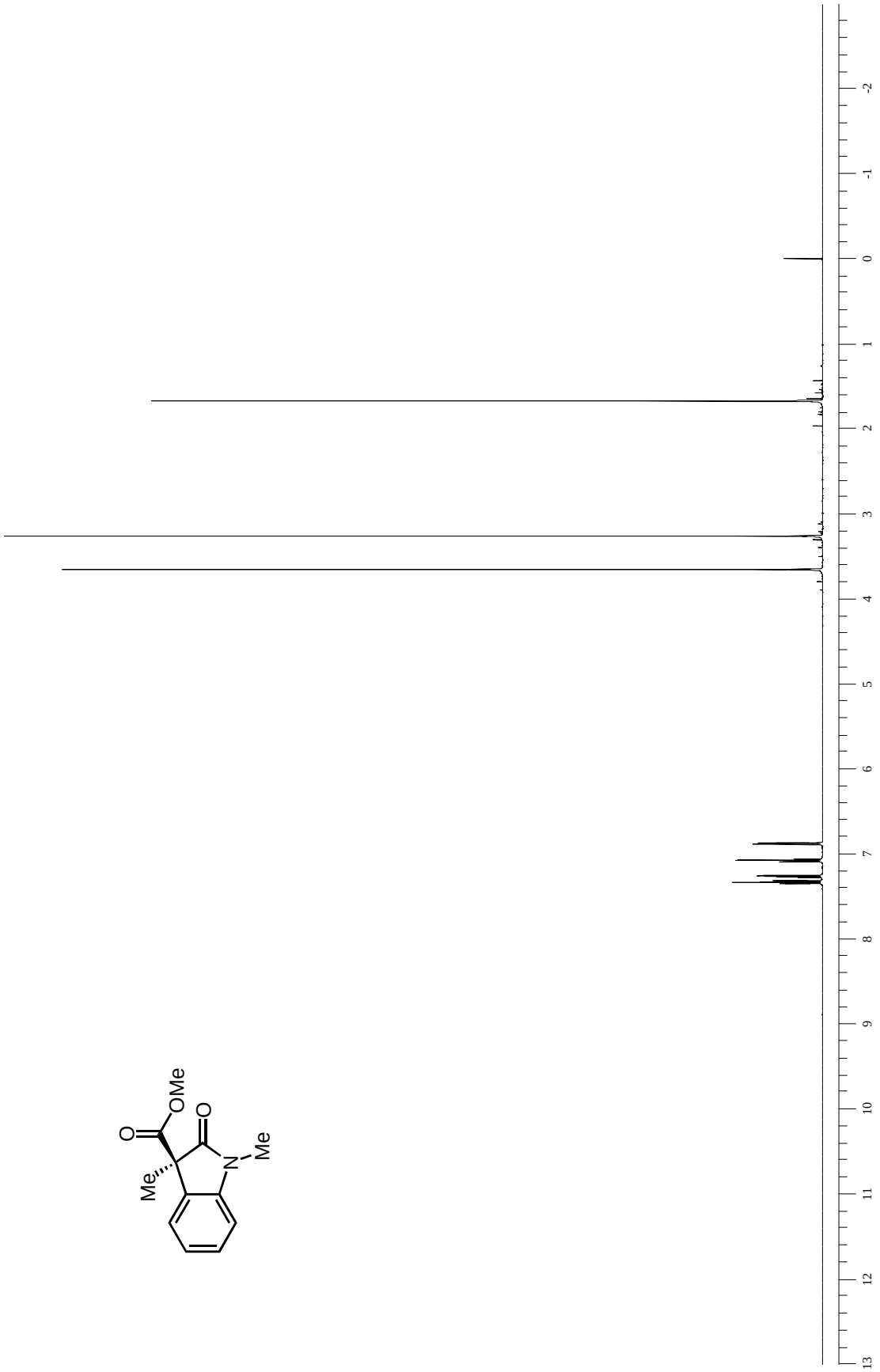
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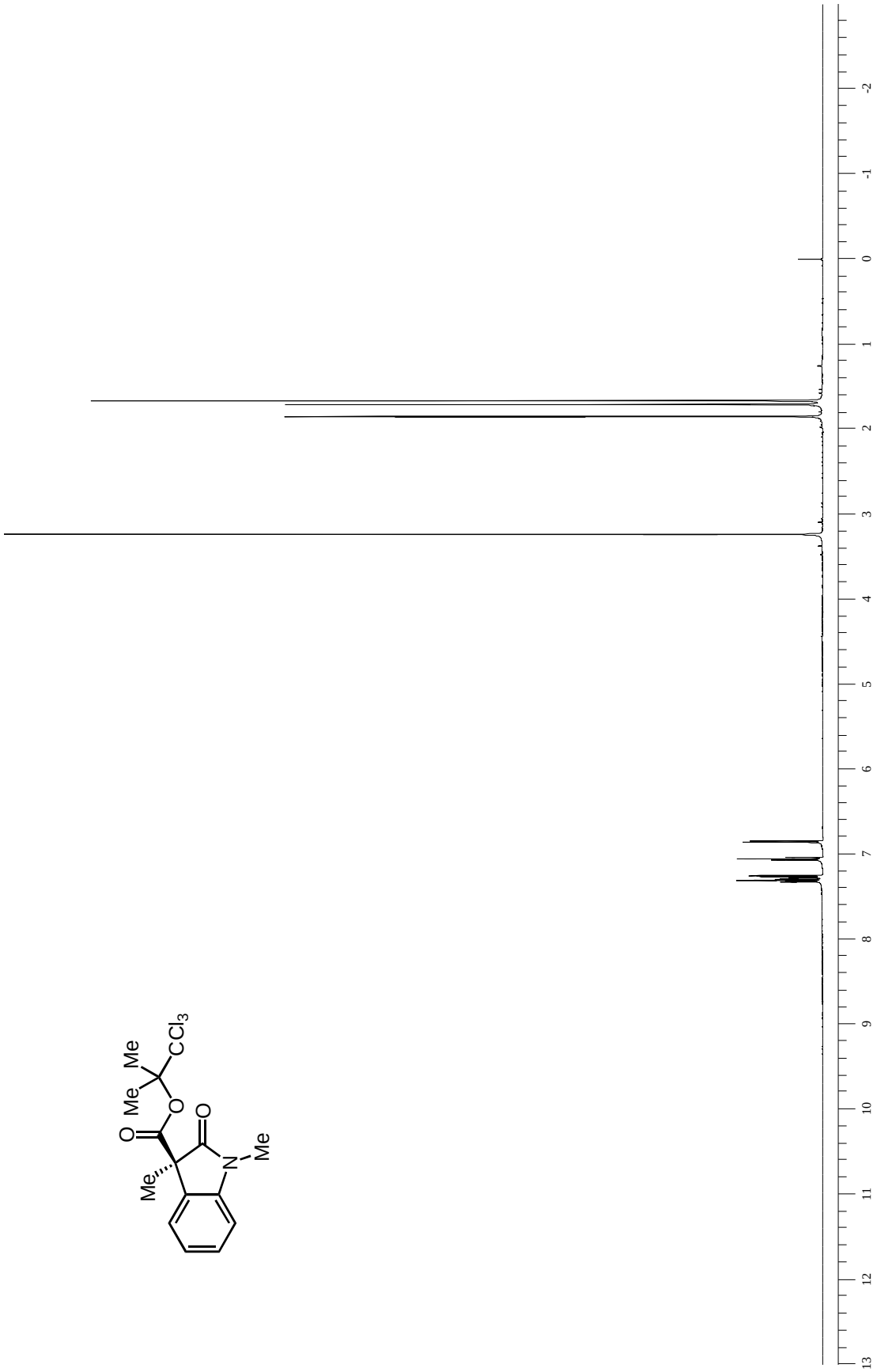
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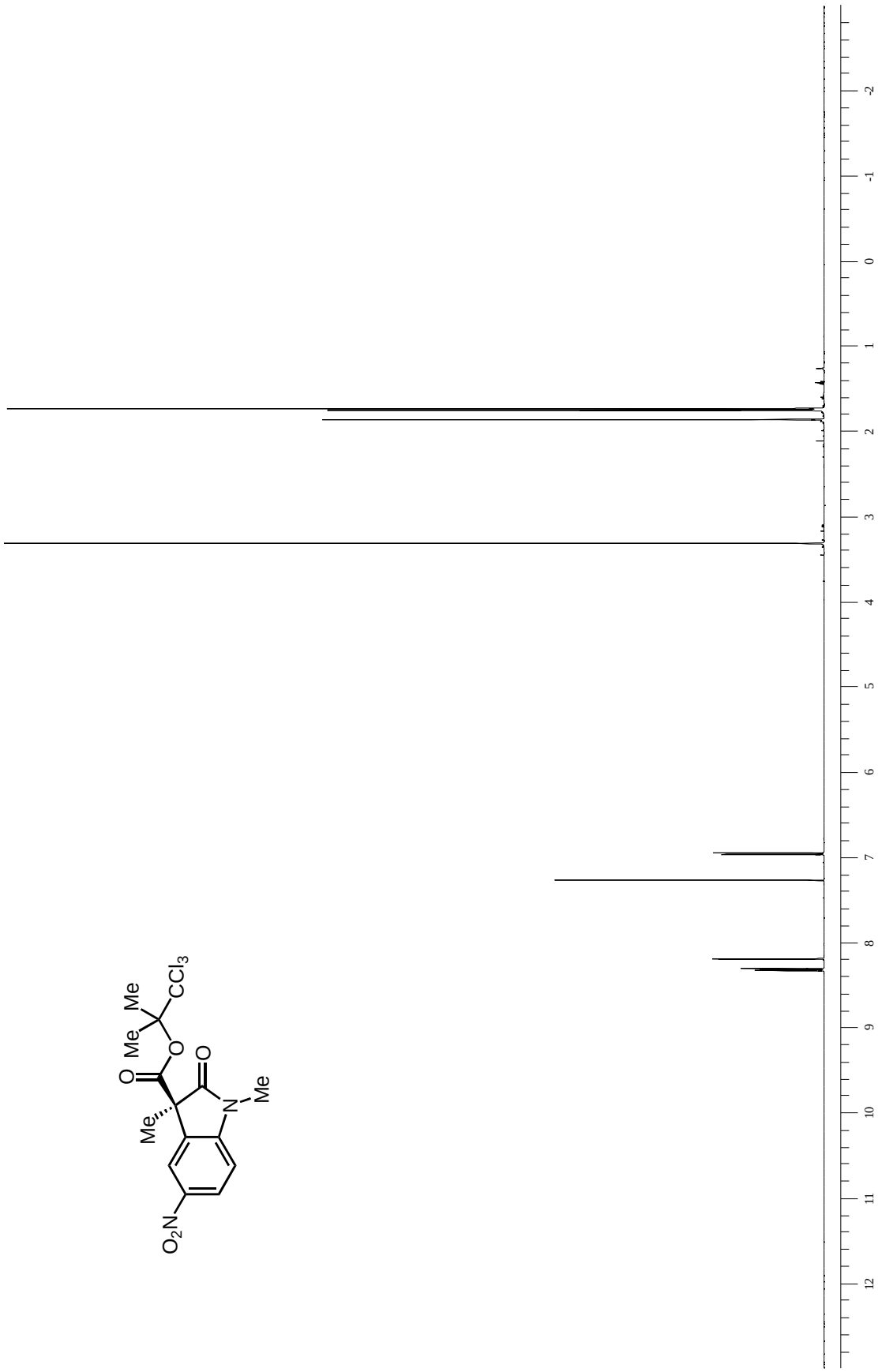
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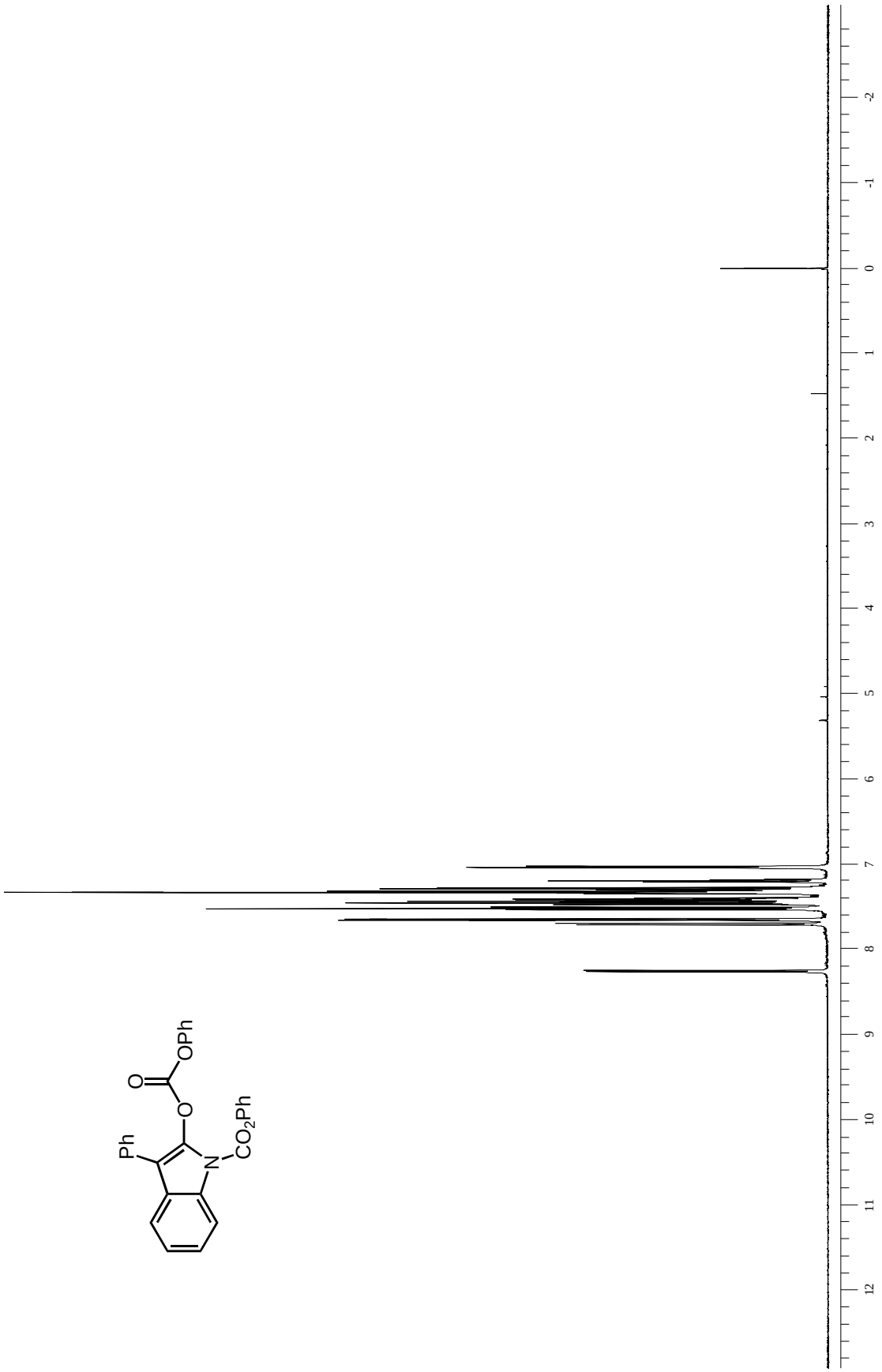
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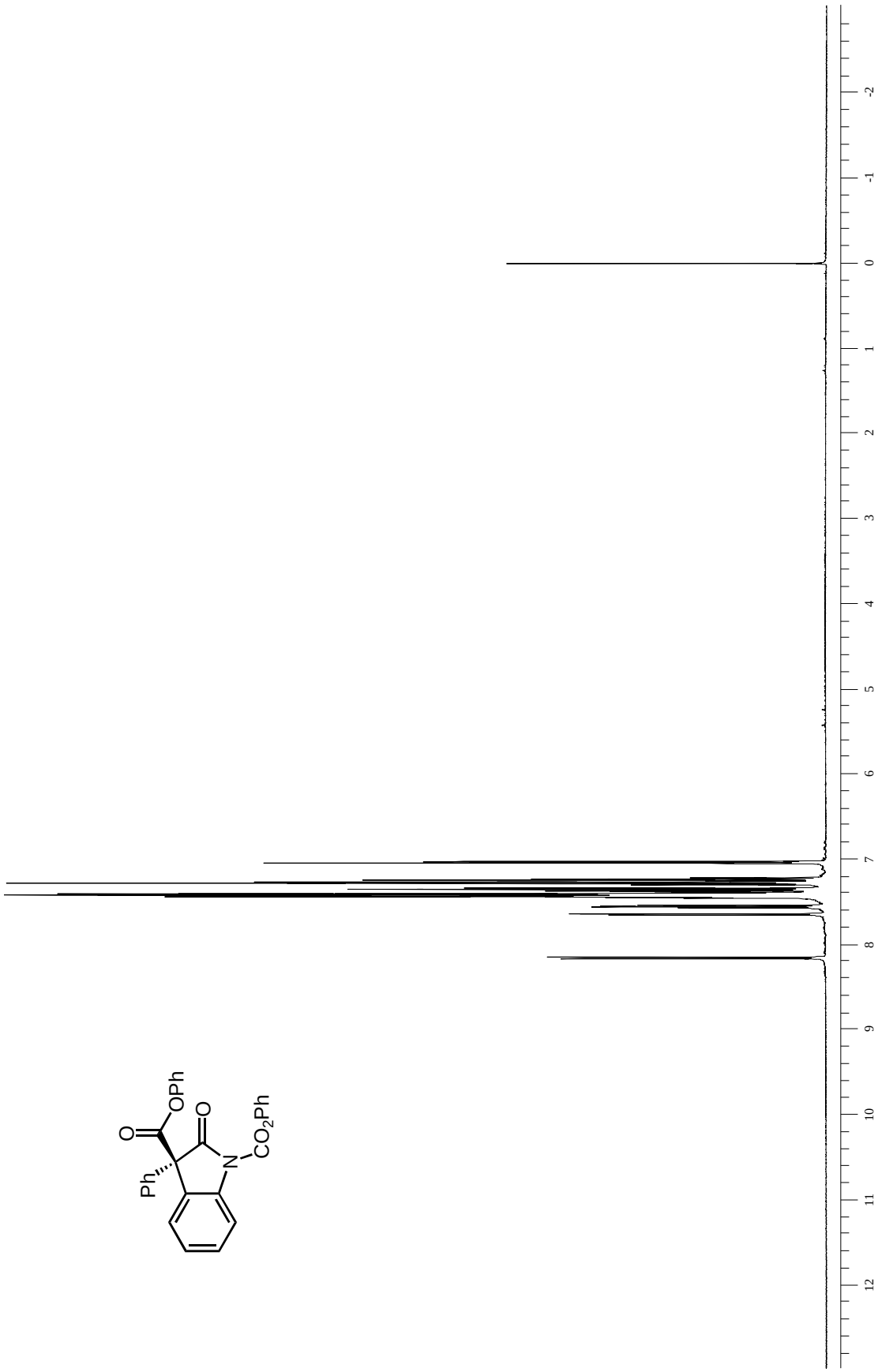
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