Rhodium-Catalyzed Chemo-, Regio-, and Enantioselestive [2+2+2] Cycloaddition of Alkynes with Isocyanates

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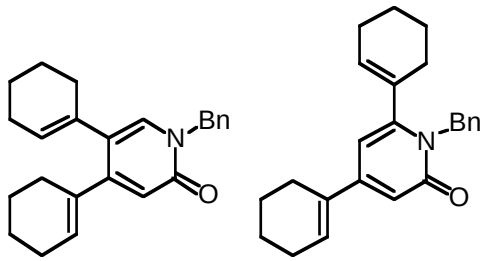
I. General

Anhydrous CH_2Cl_2 (No. 27,099-7) was obtained from Aldrich and used as received. H8-BINAP and (*R*)-DTBM-Segphos were obtained from Takasago International Corporation. All other reagents were obtained from commercial sources and used as received. All reactions were carried out under an atmosphere of argon or nitrogen in oven-dried glassware with magnetic stirring. Diynes **7a**,[1] **7b**,[2] and **7c**[3] were prepared according to literatures.

II. Rhodium-Catalyzed [2+2+2] Cycloaddition of Terminal Monoynes with Isocyanates (Table 1)

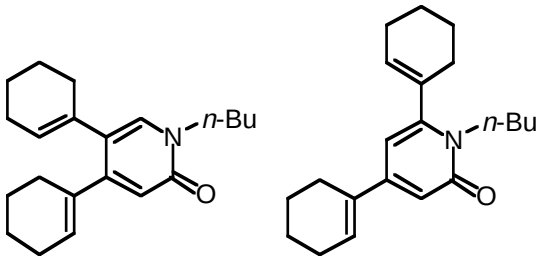
General Procedure (Table 1, entry 1). Under an Ar atmosphere, H8-BINAP (15.8 mg, 0.0250 mmol) and $[Rh(cod)_2]BF_4$ (10.2 mg, 0.0250 mmol) were dissolved in CH_2Cl_2 (1.0 mL) and the mixture was stirred at rt for 5 min. H_2 was introduced to the resulting solution in a Schlenk tube. After stirring at rt for 0.5 h, the resulting solution was concentrated to dryness and dissolved in CH_2Cl_2 (1.5 mL). To this solution was added dropwise over 1 min a solution of 1-ethynylcyclohexene (53.1 mg, 0.500 mmol) and benzyl isocyanate (133.2 mg, 1.000 mmol) in CH_2Cl_2 (0.5 mL) at rt and washed remaining substrates away by using CH_2Cl_2 (0.5 mL). The mixture was stirred at rt for 24 h. The resulting solution was concentrated and purified by preparative TLC (hexane:ethyl acetate = 2:1), which furnished a mixture of 1-benzyl-4,5-dicyclohex-1-enyl-1H-pyridin-2-one (**3aa**) and 1-benzyl-3,5-dicyclohex-1-enyl-1H-pyridin-2-one (**4aa**) (41.1 mg, 0.119 mmol, 48% yield) as a colorless oil.

1-Benzyl-4,5-dicyclohex-1-enyl-1*H*-pyridin-2-one (3aa) and 1-benzyl-3,5-dicyclohex-1-enyl-1*H*-pyridin-2-one (4aa) (entry 1, 48% yield, 3aa:4aa = 97:3).



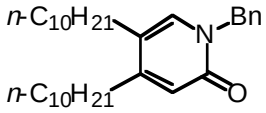
Colorless oil; IR (neat); 2900, 1640, 1580, 1420, 720, 700 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.26-7.38 (m, 5H), 6.98 (s, 1H), 6.38 (s, 1H), 5.80-5.83 (m, 1H), 5.57–5.60 (m, 1H), 5.11(s, 2H), 1.95–2.15 (m, 8H), 1.50–1.68 (m, 8H); pyridone ring protons of minor isomer **4aa**: δ 6.49 (d, J = 1.8 Hz, 1H), 6.12 (d, J = 1.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 162.3, 155.0, 136.7, 136.6, 135.4, 134.6, 128.7, 128.0, 127.8, 127.7, 126.5, 123.4, 118.0, 65.8, 51.4, 29.3, 27.9, 25.5, 25.4, 22.9, 22.7, 21.8, 21.7; HRMS (EI) calcd for $C_{24}H_{27}NO$ $[M]^+$ 345.2093, found 345.2052.

1-Butyl-4,5-dicyclohex-1-enyl-1*H*-pyridin-2-one (3ab) and 1-butyl-3,5-dicyclohex-1-enyl-1*H*-pyridin-2-one (4ab) (entry 2, 48% yield, 3ab:4ab = 97:3).



Pale yellow oil; IR (neat) 2855, 1620, 1560, 1420, 1250, 720 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 6.96 (s, 1H), 6.31 (s, 1H), 5.80 (m, 1H), 5.64 (m, 1H), 3.88 (t, J = 7.5 Hz, 2H), 2.00–2.25 (m, 8H), 1.55–1.80 (m, 10H), 1.38 (sextet, J = 7.5 Hz, 2H), 0.95 (t, J = 7.2 Hz, 3H); pyridone ring protons of minor isomer **4ab**: δ 6.39 (d, J = 1.5 Hz, 1H), 6.06 (d, J = 1.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 162.3, 154.9, 136.7, 135.5, 134.9, 127.6, 126.4, 123.2, 117.8, 49.1, 31.4, 29.4, 28.0, 25.6, 25.5, 23.0, 22.7, 21.9, 21.8, 19.9, 13.7; HRMS (EI) calcd for $C_{21}H_{29}NO$ $[M]^+$ 311.2251, found 311.2214.

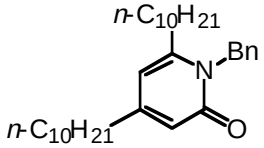
1-Benzyl-4,5-didecyl-1*H*-pyridin-2-one (3ba, entry 3, 31% yield).



Pale yellow oil; IR (neat) 2800, 1630, 1560, 1420 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.20–7.36 (m, 5H), 6.93 (s, 1H), 6.43 (s, 1H), 5.10 (s, 2H), 2.41 (t, J = 7.5 Hz, 2H),

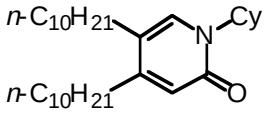
2.29 (t, J = 7.5 Hz, 2H), 1.20–1.60 (m, 32H), 0.88 (t, J = 6.6 Hz, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 162.2, 155.1, 136.9, 134.1, 128.7, 127.9, 127.7, 119.9, 118.8, 51.3, 31.94, 31.85, 30.1, 29.55, 29.49, 29.45, 29.40, 29.36, 29.28, 29.03, 28.98, 22.6, 14.1; HRMS (EI) calcd for $C_{32}H_{51}NO$ $[M]^+$ 465.3971, found 465.3982.

1-Benzyl-3,5-didecyl-1*H*-pyridin-2-one (4ba, entry 3, 30% yield).



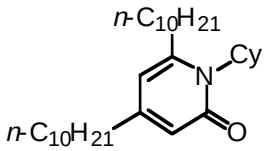
Pale yellow oil; IR (neat) 2800, 1630, 1560, 1520, 1420 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.19–7.31 (m, 3H), 7.10 (d, J = 6.9 Hz, 2H), 6.35 (d, J = 1.5 Hz, 1H), 5.89 (d, J = 1.5 Hz, 1H), 5.33 (s, 2H), 2.47 (t, J = 7.5 Hz, 2H), 2.40 (t, J = 7.5 Hz, 2H), 1.45-1.63 (m, 4H), 1.18–1.37 (m, 28H), 0.88 (t, J = 6.6 Hz, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 164.1, 154.9, 149.3, 137.1, 128.7, 127.1, 126.3, 115.5, 107.6, 46.1, 35.3, 32.8, 31.9, 31.8, 29.6, 29.5, 29.4, 29.3, 29.24, 29.22, 29.17, 28.6, 22.6, 14.1; HRMS (EI) calcd for $C_{32}H_{51}NO$ $[M]^+$ 465.3971, found 465.3977.

1-Cyclohexyl-4,5-didecyl-1*H*-pyridin-2-one (3bc, entry 4, 31% yield).



Pale yellow oil; IR (neat) 2850, 2800, 1645, 1570, 1530, 1430 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.98 (s, 1H), 6.39 (s, 1H), 4.80–4.90 (m, 1H), 2.39 (t, J = 6.0 Hz, 2H), 2.34 (t, J = 6.0 Hz, 2H), 1.85–1.92 (m, 4H), 1.20–1.60 (m, 38H), 0.88 (t, J = 5.1 Hz, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 161.8, 153.8, 130.3, 119.5, 118.3, 53.0, 32.6, 31.9, 31.8, 30.4, 29.6, 29.5, 29.4, 29.3, 29.0, 25.8, 25.5, 22.7, 14.1; HRMS (EI) calcd for $C_{31}H_{51}NO$ $[M]^+$ 457.4284, found 457.4327.

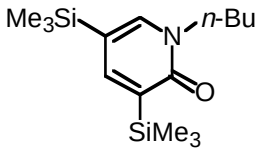
1-Cyclohexyl-3,5-didecyl-1*H*-pyridin-2-one (4bc, entry 4, 31% yield).



Pale yellow oil; IR (neat) 2860, 2810, 1645, 1570, 1510, 1440 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.14 (d, J = 1.5 Hz, 1H), 5.77 (d, J = 1.5 Hz, 1H), 3.79–3.83 (m,

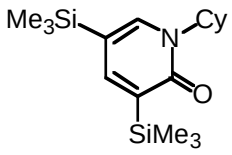
1H), 2.80–2.95(m, 2H), 2.53 (t, J = 5.7 Hz, 2H), 2.31 (t, J = 6.0 Hz, 2H), 1.20–1.35 (m, 28H), 1.48–1.65 (m, 8H), 1.86–1.90 (m, 4H), 0.884 (t, J = 5.4 Hz, 3H), 0.879 (t, J = 5.4 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 164.9, 153.6, 148.5, 117.9, 108.5, 59.9, 34.9, 34.7, 31.9, 31.8, 29.6, 29.5, 29.46, 29.4, 29.29, 29.27, 29.2, 29.1, 28.5, 26.7, 25.1, 22.6, 14.1; HRMS (EI) calcd for $C_{31}H_{51}NO$ $[M]^+$ 457.4284, found 457.4314.

1-Butyl-4,5-bis(trimethylsilanyl)-1*H*-pyridin-2-one (5cb, entry 5, 65% yield).



Brown solid; Mp 55.0–56.5 °C; IR (neat) 2850, 1605, 1230, 820 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.43 (d, J = 2.1 Hz, 1H), 7.22 (d, J = 2.1 Hz, 1H), 3.88 (t, J = 7.5 Hz, 2H), 1.60–1.77 (m, 2H), 1.33–1.45 (m, 2H), 0.96 (t, J = 7.2 Hz, 3H), 0.27 (s, 9H), 0.22 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 164.7, 149.0, 143.0, 131.4, 114.0, 49.7, 31.5, 20.1, 13.7, –1.23, –1.69; HRMS (EI) calcd for $C_{15}H_{29}NOSi_2$ $[M]^+$ 295.1788, found 295.1764.

1-Cyclohexyl-4,5-bis(trimethylsilanyl)-1*H*-pyridin-2-one (5cc, entry 6, 48% yield).



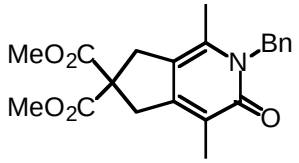
Green oil; IR (neat) 3320, 2900, 1610, 1565, 1500, 1230, 1185, 830 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.42 (d, J = 1.5 Hz, 1H), 7.32 (d, J = 1.5 Hz, 1H), 4.82–4.93 (m, 1H), 1.84–1.99 (m, 4H) 1.60–1.80 (m, 1H), 1.20-1.60 (m, 4H), 1.05–1.20 (m, 1H), 0.28 (s, 9H), 0.24 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 164.4, 148.3, 138.7, 130.8, 114.0, 53.5, 34.0, 32.7, 25.9, 25.5, 24.9, –1.18, –1.63; HRMS (EI) calcd for $C_{17}H_{31}NOSi_2$ $[M]^+$ 321.1944, found 321.1923.

III. Rhodium-Catalyzed [2+2+2] Cycloaddition of Symmetrical α,ω-Diynes with Isocyanates (Table 2)

General Procedure (Table 2, entry 1). Under an Ar atmosphere, H8-BINAP (15.8 mg, 0.0250 mmol) and $[Rh(cod)_2]BF_4$ (10.2 mg, 0.0250 mmol) were dissolved in CH_2Cl_2 (2.0 mL) and the mixture was stirred at rt for 5 min. H_2 was introduced to the resulting solution in a Schlenk tube. After stirring at rt for 0.5 h, the resulting mixture was concentrated to dryness. To the CH_2Cl_2 (3.5 mL) solution of the residue was added

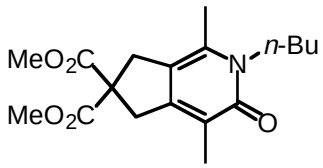
a CH_2Cl_2 (0.5 mL) solution of 2,2-dibut-2-ynylmalonic acid dimethyl ester (118.1 mg, 0.500 mmol) and benzyl isocyanate (73.2 mg, 0.550 mmol) at rt, and washed remaining substrates away by using CH_2Cl_2 (1.0 mL). The mixture was stirred at rt for 18 h. The resulting mixture was concentrated and purified by preparative TLC (hexane:ethyl acetate = 1:1), which furnished 2-benzyl-1,4-dimethyl-3-oxo-2,3,5,7-tetrahydro[2]pyrindine-6,6-dicarboxylic acid dimethyl ester (**8aa**, 183.6 mg, 0.497 mmol, 99% yield) as a colorless oil.

2-Benzyl-1,4-dimethyl-3-oxo-2,3,5,7-tetrahydro[2]pyrindine-6,6-dicarboxylic acid dimethyl ester (8aa, entry 1, 99% yield).



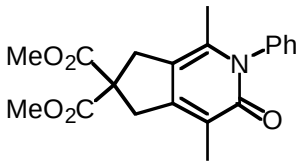
Colorless oil ; IR (neat) 3350, 2900, 1720, 1645, 1560, 1420, 1240, 1040, 720 cm^{-1};^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.20–7.32 (m, 3H), 7.12–7.15 (m, 2H), 5.32 (s, 2H), 3.77 (s, 6H), 3.45 (s, 2H), 3.36 (s, 2H) 2.17 (s, 3H), 2.11 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 171.4, 163.6, 149.4, 136.8, 136.4, 128.5, 126.9, 126.4, 119.9, 116.8, 58.9, 53.0, 47.4, 39.2, 37.6, 17.1, 13.4; HRMS (EI) calcd for $C_{21}H_{23}NO_5$ $[M]^+$ 369.1577, found 369.1580.

Butyl-1,4-dimethyl-3-oxo-2,3,5,7-tetrahydro[2]pyrindine-6,6-dicarboxylic acid dimethyl ester (8ab, entry 2, 90% yield).[1]



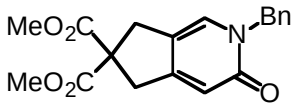
Colorless oil ; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.97 (t, J = 7.8 Hz, 2H), 3.77 (s, 6H), 3.41 (s, 2H), 3.37 (s, 2H), 2.28 (s, 3H), 2.05 (s, 3H), 1.57–1.68 (m, 2H), 1.41 (sextet, J = 7.2 Hz, 2H), 0.96 (t, J = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 171.6, 163.3, 148.8, 135.7, 120.0, 116.6, 59.1, 53.1, 44.7, 39.2, 37.9, 30.6, 20.3, 16.9, 13.7, 13.3.

2-Phenyl-1,4-dimethyl-3-oxo-2,3,5,7-tetrahydro[2]pyrindine-6,6-dicarboxylic acid dimethyl ester (8ad, entry 3, 87% yield).[1]



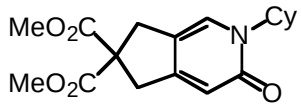
Colorless solid ; Mp 133.0-134.5 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.39–7.51 (m, 3H), 7.13–7.16 (m, 2H), 3.80 (s, 6H), 3.48 (s, 2H), 3.39 (s, 2H), 2.07 (s, 3H), 1.86 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 171.5, 163.9, 150.0, 139.4, 136.1, 129.5, 128.3, 128.0, 120.7, 116.4, 59.2, 53.1, 39.3, 37.5, 18.2, 13.1.

2-Benzyl-3-oxo-2,3,5,7-tetrahydro[2]pyrindine-6,6-dicarboxylic acid dimethyl ester (8ba, entry 4, 84% yield).[1]



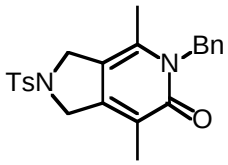
Pale yellow solid; Mp 158.0–160.0 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.26–7.37 (m, 5H), 7.08 (s, 1H), 6.49 (s, 1H), 5.08 (s, 2H), 3.75 (s, 6H), 3.42 (d, J = 1.2 Hz, 2H), 3.30 (d, J = 1.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 171.0, 162.4, 155.0, 136.6, 130.9, 128.8, 128.1, 127.9, 119.3, 114.7, 60.5, 53.1, 51.8, 39.7, 36.5.

2-Cyclohexyl-3-oxo-2,3,5,7-tetrahydro[2]pyrindine-6,6-dicarboxylic acid dimethyl ester (8bc, entry 5, 81 % yield).[1]



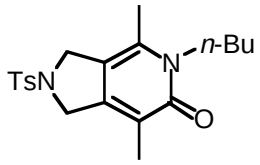
Pale yellow solid; Mp 135.0-137.0 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.17 (s, 1H), 6.40 (s, 1H), 4.81–4.88 (m, 1H), 3.76 (s, 6H), 3.42 (d, J = 1.2 Hz, 2H), 3.36 (d, J = 1.2 Hz, 2H), 1.80–1.90 (m, 4H), 1.00–1.80 (m, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 171.1, 162.0, 153.7, 127.2, 118.8, 114.1, 60.5, 53.7, 53.1, 39.7, 36.8, 33.9, 32.6, 25.7, 25.4, 24.9.

5-Benzyl-1,4-dimethyl-2-(toluene-4-sulfonyl)-1,2,3,5-tetrahydropyrrolo[3,4-*c*]pyridin-6-one (8ca, entry 6, 93% yield).



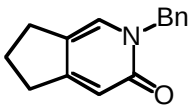
Colorless solid; Mp 99.0-100.0 °C; IR (neat) 2950, 1720, 1660, 1580, 1335, 1260, 1160,1100, 725, 700, 660 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.76–7.78 (m, 2H), 7.20–7.37 (m, 5H), 7.08–7.10 (m, 2H), 5.30 (s, 2H), 4.41 (s, 2H), 4.36 (s, 2H), 2.43 (s, 3H), 2.11(s, 3H), 2.03 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 171.3, 163.8, 149.9, 139.3, 136.0, 129.4, 128.2, 127.9, 120.5, 116.3, 59.0, 53.0, 39.1, 37.4, 18.0, 13.0; HRMS (EI) calcd for $C_{23}H_{24}N_2NaO_3S$ $[M+Na]^+$ 431.1405, found 437.1440.

5-Butyl-1,4-dimethyl-2-(toluene-4-sulfonyl)-1,2,3,5-tetrahydropyrrolo[3,4-*c*]pyridin-6-one (8cb, entry 7, 80% yield).



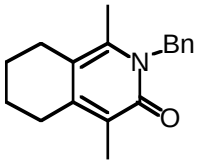
Pale yellow oil ; IR (neat) 2900, 1640, 1565, 1325, 1250, 1150, 1185, 810, 720, 655 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.75–7.78 (m, 2H), 7.34–7.36 (m, 2H), 4.37 (s, 4H), 3.95 (t, J = 7.8 Hz, 2H), 2.43 (s, 3H) , 2.22 (s, 3H), 1.94 (s, 3H), 1.53–1.63 (m, 2H), 1.33–1.45 (m, 2H), 0.95 (t, J = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 162.9, 144.8, 143.9, 135.6, 133.1, 129.9, 127.5, 119.0, 113.3, 52.2, 51.4, 44.6, 30.5, 21.5, 20.2, 17.0, 13.6, 13.2; HRMS (EI) calcd for $C_{20}H_{26}N_2NaO_3S$ $[M+Na]^+$ 397.1562, found 397.1601.

2-Benzyl-2,5,6,7-tetrahydro[2]pyrindin-3-one (8da, entry 8, 64% yield).



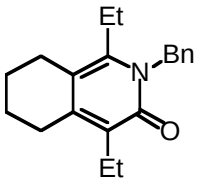
Colorless solid; Mp 99.0–100.5 °C; IR (neat) 3350, 1640, 1560, 790, 635 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.23–7.36 (m, 5H), 7.07 (s, 1H), 6.46 (s, 1H), 5.10 (s, 2H), 2.74 (dt, J = 7.5 and 1.2 Hz, 2H), 2.63 (dt, J = 7.5 and 1.2 Hz, 2H), 1.99 (quintet, J = 7.5 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 162.6, 159.6, 137.0, 130.1, 128.7, 127.9, 127.6, 123.4, 114.2, 51.6, 32.5, 28.7, 25.9; HRMS (EI) calcd for $C_{15}H_{15}NO$ $[M]^+$ 225.1154, found 225.1123.

2-Benzyl-1,4-dimethyl-5,6,7,8-tetrahydro-2*H*-isoquinolin-3-one (8ea, entry 9, 85% yield).



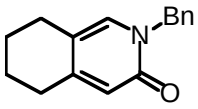
Pale yellow oil; IR (neat) 2850, 1720, 1610, 1550, 1520, 1410, 1230, 720 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.18–7.31 (m, 3H), 7.12–7.18 (m, 2H), 5.43 (s, 2H), 2.55–2.65 (m, 2H), 2.40–2.50 (m, 2H), 2.16 (s, 3H), 2.13 (s, 3H), 1.68–1.78 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 162.4, 146.8, 138.8, 137.1, 128.5, 126.9, 126.3, 122.1, 113.8, 47.8, 28.0, 26.3, 22.9, 22.3, 15.5, 12.3; HRMS (EI) calcd for $C_{18}H_{21}NO$ $[M]^+$ 267.1624, found 267.1569.

2-Benzyl-1,4-diethyl-5,6,7,8-tetrahydro-2*H*-isoquinolin-3-one (8fa, entry 10, 98% yield).



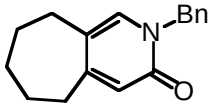
Colorless solid; Mp 159.0-160.0 °C; IR (neat) 2900, 1620, 1520, 1250, 700 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.24–7.38 (m, 2H), 7.18–7.24 (m, 1H), 7.07–7.13 (m, 2H), 5.43 (s, 2H), 2.45–2.70 (m, 4H), 2.55–2.65 (m, 2H), 2.40–2.50 (m, 2H), 1.65–1.80 (m, 4H), 1.10 (t, H = 7.6 Hz, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 162.0, 146.3, 143.9, 137.7, 128.6, 128.4, 126.9, 126.2, 113.4, 47.0, 27.0, 25.3, 22.9, 22.4, 22.2, 19.9, 12.3; HRMS (EI) calcd for $C_{20}H_{25}NO$ $[M]^+$ 295. 1936, found 295.1905.

2-Benzyl-5,6,7,8-tetrahydro-2*H*-isoquinolin-3-one (8ga, entry 11, 65% yield).



Pale yellow oil; IR (neat) 3300, 2800, 1620, 1550, 1410, 1320, 1230, 1140, 1050, 830, 680 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.24–7.35 (m, 5H), 6.96 (s, 1H), 6.35 (s, 1H), 5.10 (s, 2H), 2.57–2.65 (m, 2H), 2.40–2.48 (m, 2H), 1.65–1.75 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 161.9, 151.9, 136.8, 134.1, 128.7, 128.0, 127.7, 118.1, 116.6, 51.3, 28.8, 25.3, 22.6, 22.1; HRMS (EI) calcd for $C_{16}H_{17}NO$ $[M]^+$ 239.1310, found 239.1261.

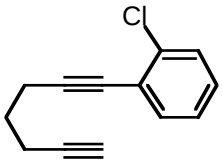
2-Benzyl-2,5,6,7,8,9-hexahydrocyclohepta[*c*]pyridin-3-one (8ha, entry 12, 48% yield).



Colorless solid; Mp 128.0–129.5 °C; IR (neat) 2950, 1660, 1590, 1270, 740 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.25–7.37 (m, 5H), 6.95 (s, 1H), 6.39 (s, 1H), 5.09 (s, 2H), 2.56–2.61 (m, 2H), 2.42–2.46 (m, 2H), 1.52–1.78 (m, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 162.4, 157.2, 136.9, 133.5, 128.7, 128.0, 127.8, 122.4, 118.6, 51.1, 36.3, 32.3, 31.9, 29.5, 28.2; HRMS (EI) calcd for $C_{17}H_{19}NO$ $[M]^+$ 253.1467, found 253.1447.

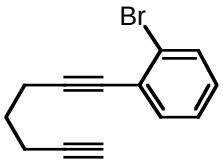
IV. Synthesis of Unsymmetrical α,ω-Diynes (Tables 3)

1-Chloro-2-hehpta-1,6-diynylbenzene (9a). To a solution of 2-chrolo-1-iodobenzene (9.3 g, 0.039 mol) and 1,6-heptadiyne (3.0 g, 0.033 mol) in Et_3N (35 mL) was added $PdCl_2(PPh_3)_2$ (0.21 g, 0.030 mmol). The mixture was then stirred at rt for 5 min, and CuI (57 mg, 0.030 mmol) was added. The resulting mixture was heated under a N_2 atmosphere at 50 °C for 5 h and stirred at rt over night. The resulting mixture was filtered, concentrated, and purified by silica gel chromatography (hexane), which furnished 1-chloro-2-hepta-1,6-diynylbenzene (**9a**, 2.0 g, 0.034 mmol, 86%) as a colorless oil.



Colorless oil; IR (neat) 3250, 2900, 1460, 1420, 1060, 740 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.40–7.46 (m, 1H), 7.34–7.39 (m, 1H), 7.14–7.24 (m, 2H), 2.62 (t, J = 6.6 Hz, 2H), 2.43 (dt, J = 6.9 and 2.7 Hz, 2H), 1.99 (t, J = 2.7 Hz, 1H), 1.87 (quintet, J = 6.9 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 135.7, 133.2, 129.1, 126.7, 126.3, 123.5, 94.6, 83.5, 78.2, 68.9, 27.5, 18.6, 17.5; HRMS (EI) calcd for $C_{13}H_{11}Cl$ $[M]^+$ 202.0550, found 202.0526.

1-Bromo-2-hehpta-1,6-diynylbenzene (9b). The title compound was prepared as a colorless oil in 48% isolated yield from 2-bromo-1-iodobenzene and 1,6-heptadiyne according to the procedure of **9a**.

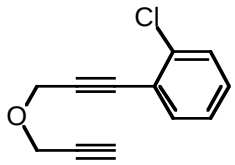


Colorless oil; IR (neat) 3250, 2900, 1420, 1250, 1100, 720, 620 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.56 (dd, J = 7.8 and 1.2 Hz, 1H), 7.42 (dd, J = 7.8 and 1.2 Hz, 1H), 7.24 (dt, J = 7.8 and 1.2 Hz, 1H), 7.12 (dt, J = 7.8 and 1.2 Hz, 1H), 2.61 (t, J = 6.9 Hz, 2 H), 2.46 (dt, J = 6.9 and 2.4 Hz, 2H), 1.99 (t, J = 2.4 Hz, 1H), 1.87 (quintet, J = 6.9 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 133.2, 133.1, 132.1, 128.8, 126.8, 125.4, 94.0, 83.5, 80.0, 68.9, 27.5, 18.7, 17.7; HRMS (EI) calcd for $C_{13}H_{11}Br$ $[M]^+$ 246.0044,

found 246.0001.

1-Chloro-2-(3-prop-2-ynyloxyprop-1-ynyl)benzene (9c). To a solution of 2-chrolo-1-iodobenzene (9.5 g, 0.040 mol) and propargyl alcohol (2.7 g, 0.048 mol) in Et_3N (150 mL) was added $PdCl_2(PPh_3)_2$ (0.28 g, 0.40 mmol) at rt. The mixture was then stirred at rt for 5 min, and CuI (76 mg, 0.40 mmol) was added. The resulting mixture was stirred under a N_2 atmosphere at 50 °C for 5 h and stirred at rt over night. The resulting mixture was filtered, concentrated, and purified by silica gel chromatography (hexane:ethyl acetate = 10:1), which furnished 3-(2-chlorophenyl)prop-2-yn-1-ol (5.7 g, 0.034 mmol, 86% yield) as a brown liquid.

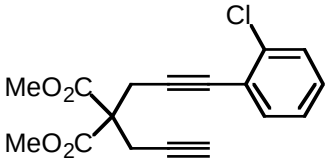
To a stirred suspension of sodium hydride (0.33 g, 0.014 mol) in THF (30 ml) was added a THF (5.0 mL) solution of 3-(2-chlorophenyl)prop-2-yn-1-ol (2.0 g, 0.012 mol) at rt, and the resulting mixture was stirred at rt for 10 min. Propargyl bromide (80% in toluene, 2.2 g, 0.018 mol) was added, and the resulting mixture was stirred at rt overnight. The reaction mixture was extracted with ether. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated. The crude product was purified by silica gel column chromatography (hexane:ethyl acetate = 20:1) afforded 1-chloro-2-(3-prop-2-ynyloxyprop-1-ynyl)benzene (**9c**, 1.73 g, 8.45 mmol, 70% yield) as a pale yellow oil.



Pale yellow oil; IR (neat) 3250, 2900, 1420, 1330, 1060, 740 c m^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.48 (dd, J = 7.2 and 2.1 Hz, 1H), 7.35–7.42 (m, 1H), 7.17–7.31 (m, 2H), 4.55 (s, 2H), 4.38 (d, J = 2.4 Hz, 2H), 2.48 (t, J = 2.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 133.5, 133.4, 129.6, 129.2, 126.5, 126.4, 89.3, 83.6, 78.9, 75.0, 57.2, 56.5; HRMS (EI) calcd for $C_{12}H_9ClO$ $[M]^+$ 204.6520, found 204.6512.

2-[3-(Chlorophenyl)prop-2-ynyl]-2-prop-2-ynylmolonic acid dimethyl ester (9d).

To a MeOH (10 mL) solution of NaOMe (176 mg, 3.27 mmol) was added a MeOH (3.0 mL) solution of 2-(2-propynyl)malonic acid dimethyl ester (370 mg, 2.18 mmmol) and a MeOH (3.0 mL) solution of 1-(3-bromo-1-propynyl)-2-chlorobenzene (600 mg, 2.61 mmol). The resulting mixture was refluxed for 5 h. The reaction was quenched by the addition of water and extracted with Et_2O. The organic layer was washed with brine, dried over Na_2SO_4, concentrated, and purified by silica gel chromatography (hexane:ethyl acetate = 10:1), which furnished 2-[3-(chlorophenyl)prop-2-ynyl]-2-prop-2-ynylmolonic acid dimethyl ester (**9d**, 580 mg, 1.82 mmol, 83% yield) as a colorless oil.

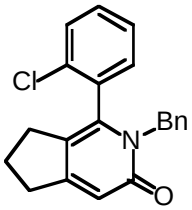


Colorless oil; IR (neat) 3250, 2950, 1730, 1420, 1200, 1160, 950, 740 c m^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.32–7.44 (m, 1H), 7.32–7.39 (m, 1H), 7.15–7.29 (m, 2H), 3.79 (s, 6H), 3.29 (s, 2H), 3.11 (d, J = 2.7 Hz, 2H), 2.07 (t, J = 2.7 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 169.1, 135.8, 133.4, 129.1, 126.3, 122.8, 89.2, 80.5, 78.5, 71.8, 56.7, 53.2, 23.8, 22.9; HRMS (EI) calcd for $C_{17}H_{15}ClO_4$ $[M]^+$ 318.0659, found 318.0650.

V. Rhodium-Catalyzed [2+2+2] Cycloaddition of Unsymmetrical α,ω–Diynes with Isocyanates (Table 3)

General Procedure (Table 3, entry 1). Under an Ar atmosphere, (*R*)-DTBM-Segphos (29.5 mg, 0.0250 mmol) and $[Rh(cod)_2]BF_4$ (10.2 mg, 0.0250 mmol) were dissolved in CH_2Cl_2 (3.0 mL) and the mixture was stirred at rt for 5 min. H_2 was introduced to the resulting solution in a Schlenk tube. After stirring at rt for 0.5 h, the resulting mixture was concentrated to dryness. To the CH_2Cl_2 (3.5 mL) solution of the residue was added a CH_2Cl_2 (0.5 mL) solution of 1-chloro-2-hehpta-1,6-diynylbenzene (101.3 mg, 0.500 mmol) and benzyl isocyanate (133.2 mg, 1.000 mmol) below –20 °C, and washed remaining substrates away by using CH_2Cl_2 (1.0 mL). The solution was kept at –20 °C for 12 h. The resulting solution was concentrated and purified by preparative TLC (hexane:ethyl acetate = 2:1), which furnished (+)-2-butyl-1-(2-chlorophenyl)-2,5,6,7-tetrahydro[2]pyrindin-3-one [(+)-**10aa**, 135.5 mg, 0.4035 mmol, 81% yield] as a colorless oil.

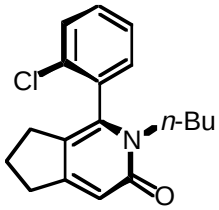
(+)-2-Benzyl-1-(2-chlorophenyl)-2,5,6,7-tetrahydro[2]pyrindin-3-one [(+)-10aa, entry 1, 81% yield, 87% ee].



Colorless oil; $[\alpha]^{25}_D$ +26.2 (acetone, *c* 2.22, 87% ee); IR (neat) 3350, 2900, 1645, 1570, 1555, 1420, 710 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.44 (dd, J = 8.1 and 0.9 Hz, 1H), 7.30–7.37 (m, 1H), 7.08–7.17 (m, 4H), 6.78–6.85 (m, 3H), 6.60 (s, 1H), 5.53 (d, J = 15.3 Hz, 1H), 4.57 (d, J = 15.3 Hz, 1H), 2.79–2.91 (m, 2H), 2.21–2.38 (m, 2H), 1.88-2.00 (m, 2H) ; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 163.4, 158.7, 139.3, 137.4, 133.4, 132.8, 131.0, 130.5, 129.6, 128.1, 127.1, 126.9, 126.7, 123.4, 114.0, 48.1, 32.9, 29.4, 25.1; HRMS (EI) calcd for $C_{21}H_{18}ClNO$ $[M]^+$ 335.1077, found 335.1083. CHIRALPAK

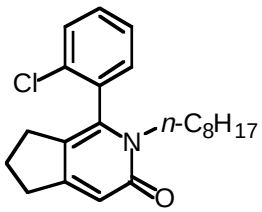
AD, hexane:2-PrOH = 96:4, 0.9 mL/min, retention times: 58.1 min (minor isomer) and 62.4 min (major isomer).

(*R*)-(+)-2-Butyl-1-(2-chlorophenyl)-2,5,6,7-tetrahydro[2]pyrindin-3-one [(*R*)-(+)-10ab, entry 2, 79% yield, 88% ee].



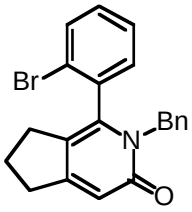
Reaction time: 12 h; Colorless solid; Mp 86.5-87.5 °C; $[\alpha]^{25}_{D}$ +23.3 (acetone, *c* 0.748 , 88% ee); IR (neat) 3300, 2855, 1640, 1550, 1420, 1250, 720 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.46–7.55 (m, 1H), 7.27–7.44 (m, 2H), 7.20–7.26 (m, 1H), 6.49 (s, 1H), 3.98 (ddd, *J* = 15.9, 10.8, and 5.1 Hz, 1H), 3.44 (ddd, *J* = 15.9, 10.8, and 5.1 Hz, 1H), 2.82 (t, *J* = 7.5 Hz, 2H), 2.20–2.40 (m, 2H), 1.88–2.05 (m, 2H), 1.53–1.65 (m, 1H), 1.30–1.45 (m, 1H), 1.05–1.20 (m, 2H), 0.70 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ163.0, 158.0, 139.2, 133.5, 133.3, 130.6, 130.5, 129.9, 127.1, 123.0, 113.9, 45.4, 32.8, 30.6, 29.5, 25.2, 19.9, 13.4; HRMS (EI) calcd for $C_{18}H_{20}ClNO$ $[M]^+$ 301.1233, found 301.1204. CHIRALPAK AD, hexane:2-PrOH = 85:15, 1.0 mL/min, retention times: 10.2 min (major isomer) and 12.2 min (minor isomer). The absolute configuration was determined to be *R* by anomalous dispersion method.

(+)-2-Octyl-1-(2-chlorophenyl)-2,5,6,7-tetrahydro[2]pyrindin-3-one [(+)-10ae, entry 3, 78% yield, 90% ee].



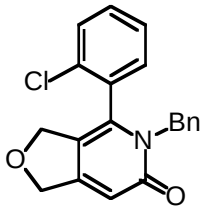
Reaction time: 12 h; Colorless oil; $[\alpha]^{25}_{D}$ +23.4 (acetone, *c* 0.222, 90% ee); IR (neat) 3300, 2850, 1640, 1560, 1420, 840, 740 cm^{-1}; δ 7.45–7.54 (m, 1H), 7.36–7.43 (m, 2H), 7.27–7.30 (m, 1H), 6.49 (s, 1H), 3.94 (ddd, *J* = 15.9, 10.8, and 5.1 Hz, 1H), 3.43 (ddd, *J* = 15.9, 10.8, and 5.1 Hz, 1H), 2.82 (t, *J* = 7.5 Hz, 2H), 2.22–2.40 (m, 2H), 1.86–2.00 (m, 2H), 1.55–1.68 (m, 1H), 1.30–1.45 (m, 1H), 1.05–1.26 (m, 10H), 0.84 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 163.0, 158.0, 139.1, 133.5, 133.4, 130.6, 130.5, 129.9, 127.0, 122.9, 113.9, 45.7, 32.8, 31.6, 29.5, 28.9, 28.7, 28.4, 26.6, 25.1, 22.5, 14.0; HRMS (EI) calcd for $C_{22}H_{28}ClNO$ $[M–Cl]^+$ 322.2170, found 322.2194. CHIRALPAK AD, hexane:2-PrOH = 96:4, 1.0 mL/min, retention times: 31.3 min (major isomer) and 35.6 min (minor isomer).

(+)-2-Benzyl-1-(2-bromophenyl)-2,5,6,7-tetrahydro[2]pyrindin-3-one [(+)-10ba, entry 4, 83% yield, 85% ee].



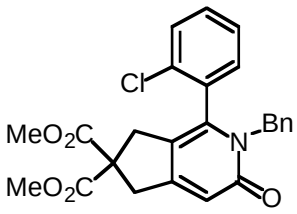
Reaction time: 12 h; Colorless oil; $[\alpha]^{25}_{D}$ +17.0 (acetone, *c* 1.349, 85% ee); IR (neat) 3400, 2950, 1650, 1560, 1420, 1230, 1200, 850, 760, 720 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.63 (dd, *J* = 7.8 and 1.2 Hz, 1H), 7.25 (dt, *J* = 11.7 and 1.2 Hz, 2H), 7.13–7.20 (m, 3H), 6.75–6.88 (m, 3H), 6.61 (s, 1H), 5.58 (d, *J* = 15.0 Hz, 1H), 4.49 (d, *J* = 15.0 Hz, 1H), 2.85 (t, *J* = 7.8 Hz, 2H), 2.13–2.38 (m, 2H), 1.90–2.04 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 163.3, 158.7, 140.8, 137.4, 134.8, 132.7, 131.1, 130.5, 128.1, 127.2, 127.1, 126.9, 123.4, 123.2, 114.0, 48.2, 32.9, 29.4, 25.1; HRMS (EI) calcd for $C_{21}H_{18}BrNO$ $[M–Br]^+$ 300.1389, found 300.1364. CHIRALPAK AD, hexane:2-PrOH = 96:4, 1.0 mL/min, retention times: 55.0 min (minor isomer) and 59.9 min (major isomer).

(+)-5-Benzyl-4-(2-chlorophenyl)-3,5-dihydro-1*H*-furo[3,4-*c*]pyrindin-6-one [(+)-10ca, entry 5, 58% yield, 91% ee].



Reaction time: 15 h; Colorless oil; $[\alpha]^{25}_{D}$ +24.1 (acetone, *c* 0.928 , 91% ee); IR (neat) 3300, 1640, 1570, 715 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.47 (dd, *J* = 8.1 and 1.2 Hz, 1H), 7.38 (dt, *J* = 7.5 and 1.5 Hz, 1H), 7.10–7.22 (m, 4H), 6.78–6.90 (m, 3H), 6.60 (s, 1H), 5.56 (d, *J* = 15.0 Hz, 1H), 4.97 (s, 2H), 4.59 (d, *J* = 15.0 Hz, 1H), 4.51 (d, *J* = 15.0 Hz, 1H), 4.47 (d, *J* = 15.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 163.2, 153.4, 136.9, 133.1, 131.7, 131.2, 130.6, 129.9, 128.2, 127.2, 127.1, 127.0, 119.2, 111.0, 72.2, 70.5, 48.2; HRMS (EI) calcd for $C_{20}H_{16}ClNO_2$ $[M]^+$ 337.0870, found 337.0877. CHIRALPAK OD-H, hexane:2-PrOH = 72:28, 0.8 mL/min, retention times: 8.9 min (major isomer) and 10.8 min (minor isomer).

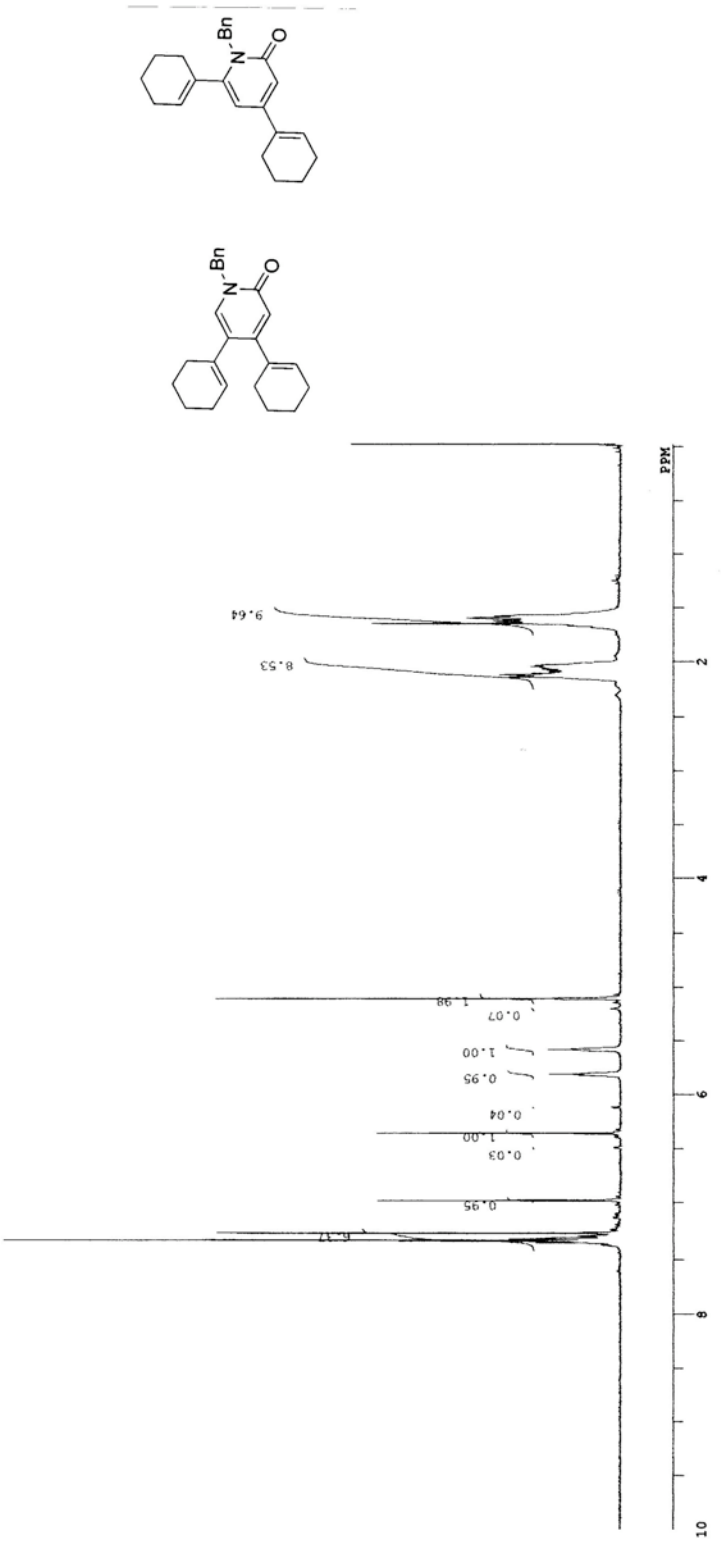
(+)-2-Benzyl(2-chlorophenyl)-3-oxo-2,3,5,7-tetrahydro[2]pyrindine-6,6-dicarboxylic acid dimethyl ester [(+)-10da, entry 6, 89% yield, 92% ee].



Reaction time: 36 h; Colorless oil; $[\alpha]^{25}_{D}$ +35.8 (acetone, *c* 0.754, 92% ee); IR (neat) 3300, 1720, 1660, 1600, 1410, 1250 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.45 (dd, *J* = 8.1 and 1.5 Hz, 1H), 7.37 (dt, *J* = 8.1 and 1.5 Hz, 1H), 7.09–7.20 (m, 4H), 6.86 (dd, *J* = 8.1 and 1.5 Hz, 1H), 6.79–6.83 (m, 2H), 6.59 (s, 1H), 5.47 (d, *J* = 15.3 Hz, 1H), 4.58 (d, *J* = 15.3 Hz, 1H), 3.72 (s, 3H), 3.71 (s, 3H), 3.58 (dd, *J* = 17.4 and 1.5 Hz, 1H), 3.44 (dd, *J* = 17.4 and 1.5 Hz, 1H), 2.97 (d, *J* = 16.2 Hz, 1H), 2.90 (d, *J* = 16.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 171.1, 170.9, 163.2, 154.1, 140.2, 137.0, 133.3, 132.1, 130.9, 130.8, 129.8, 128.1, 127.2, 127.1, 126.9, 119.5, 114.4, 59.9, 53.1, 53.0, 48.2, 40.0, 37.2; HRMS (EI) calcd for $C_{25}H_{22}ClNO_5$ $[M]^+$ 451.1187, found 451.1188. CHIRALPAK OD-H, hexane:2-PrOH = 50:50, 0.6 mL/min, retention times: 9.4 min (major isomer) and 12.6 min (minor isomer).

VI. References

1) Duong, H. A.; Cross, M. J.; Louie, J. *J. Am. Chem. Soc*. **2004**, *126*, 11438–11439.
2) Yamamoto, Y.; Kinpara, K.; Saigoku, T.; Takagishi, H.; Okuda, S.; Nishiyama, H.; Ito, K. *J. Am. Chem. Soc*. **2005**, *127*, 605–613.
3) Atkinson, R. S.; Grimshire, M. J. *J. Chem. Soc., Perkin Trans. 1* **1986**. *7*, 1215–1224.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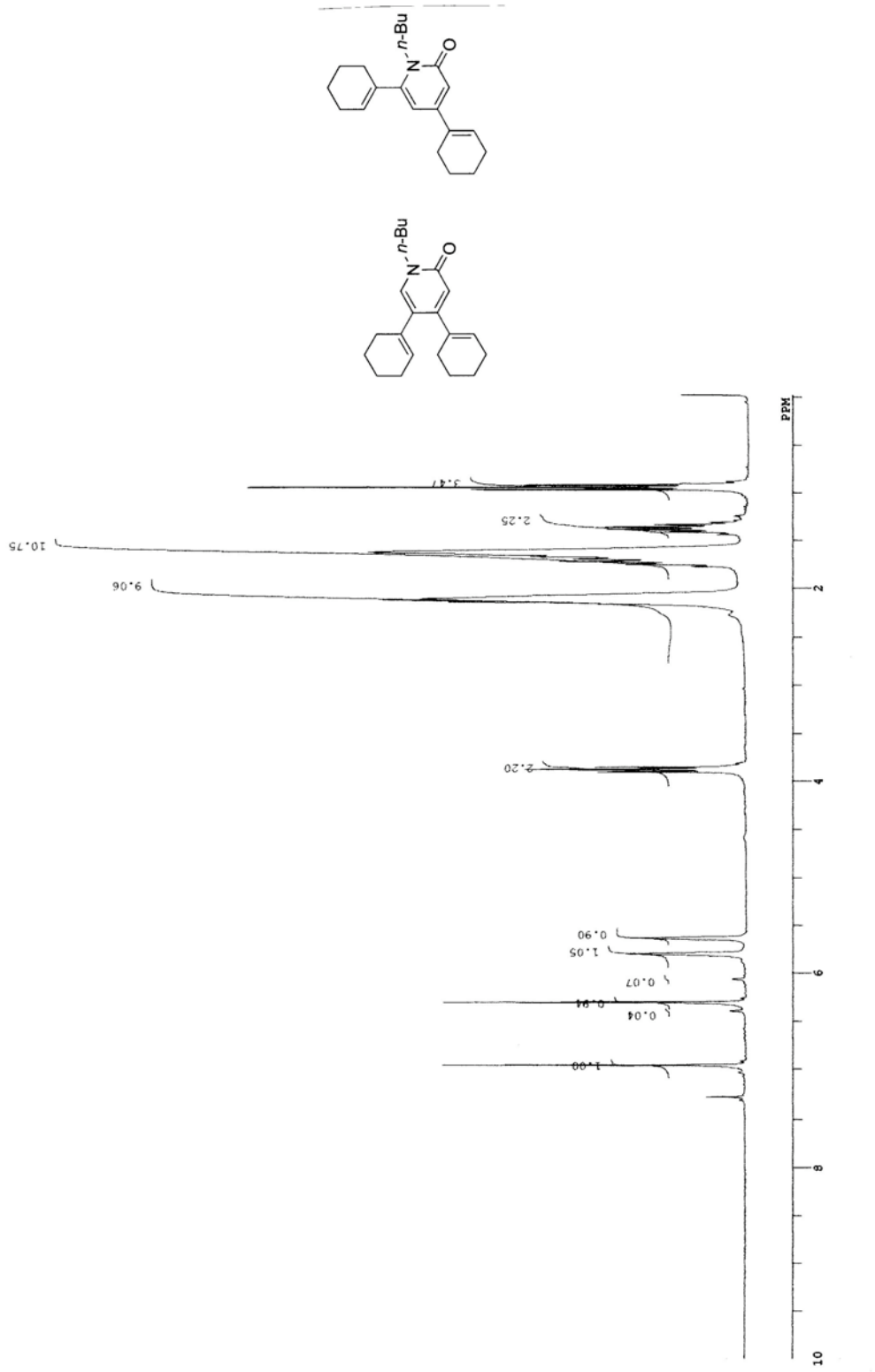
4
6
8
10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8
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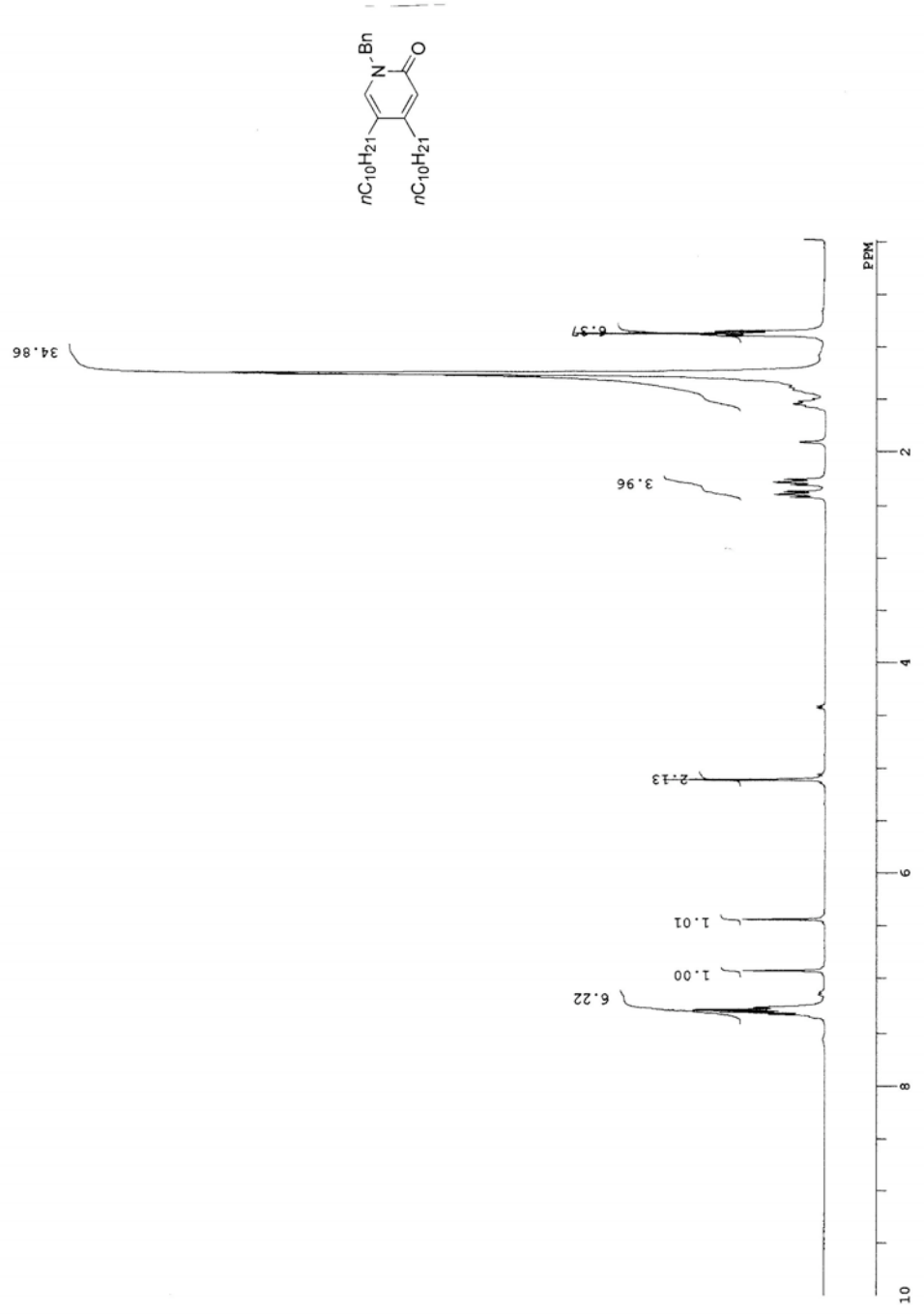
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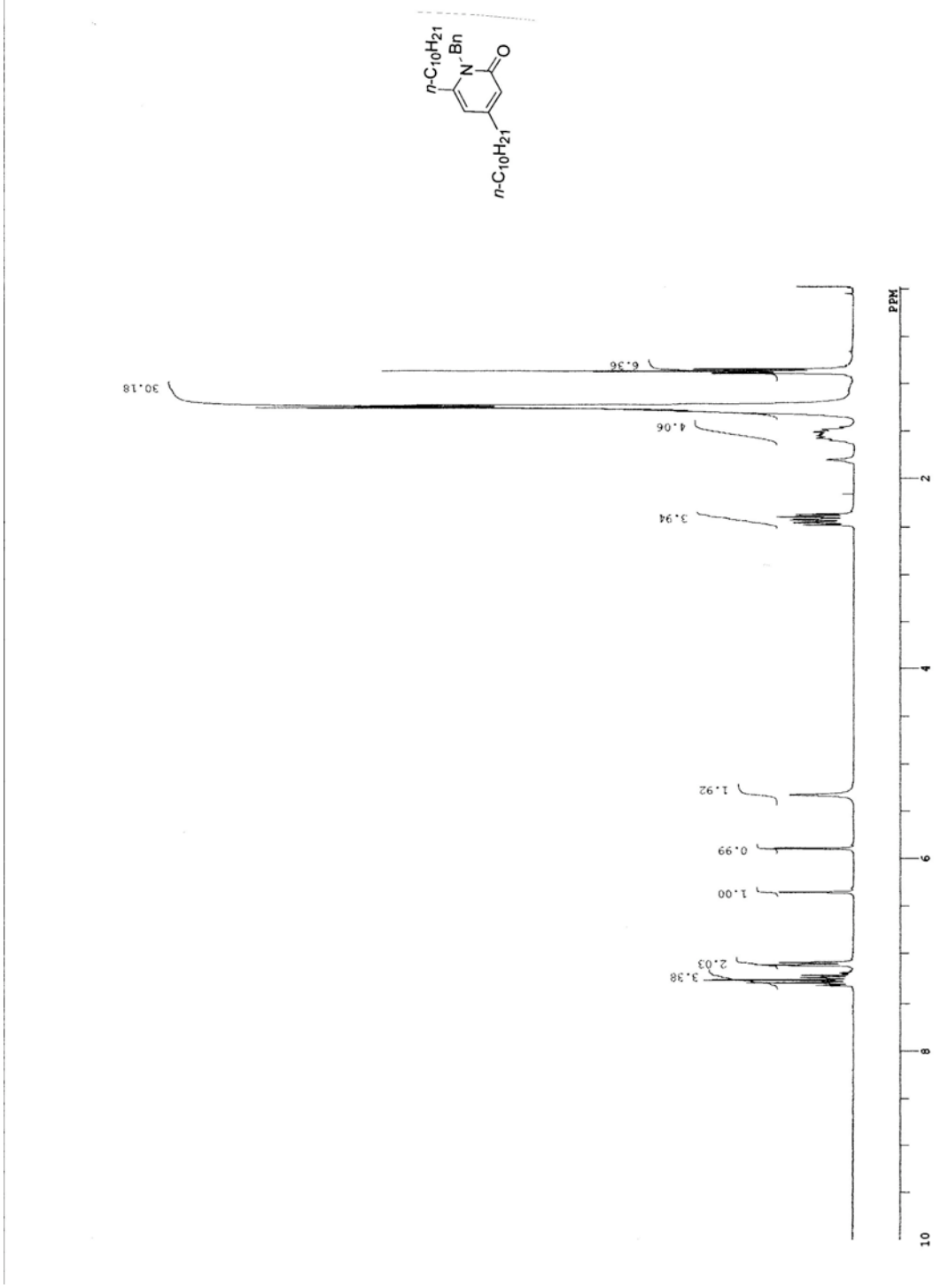
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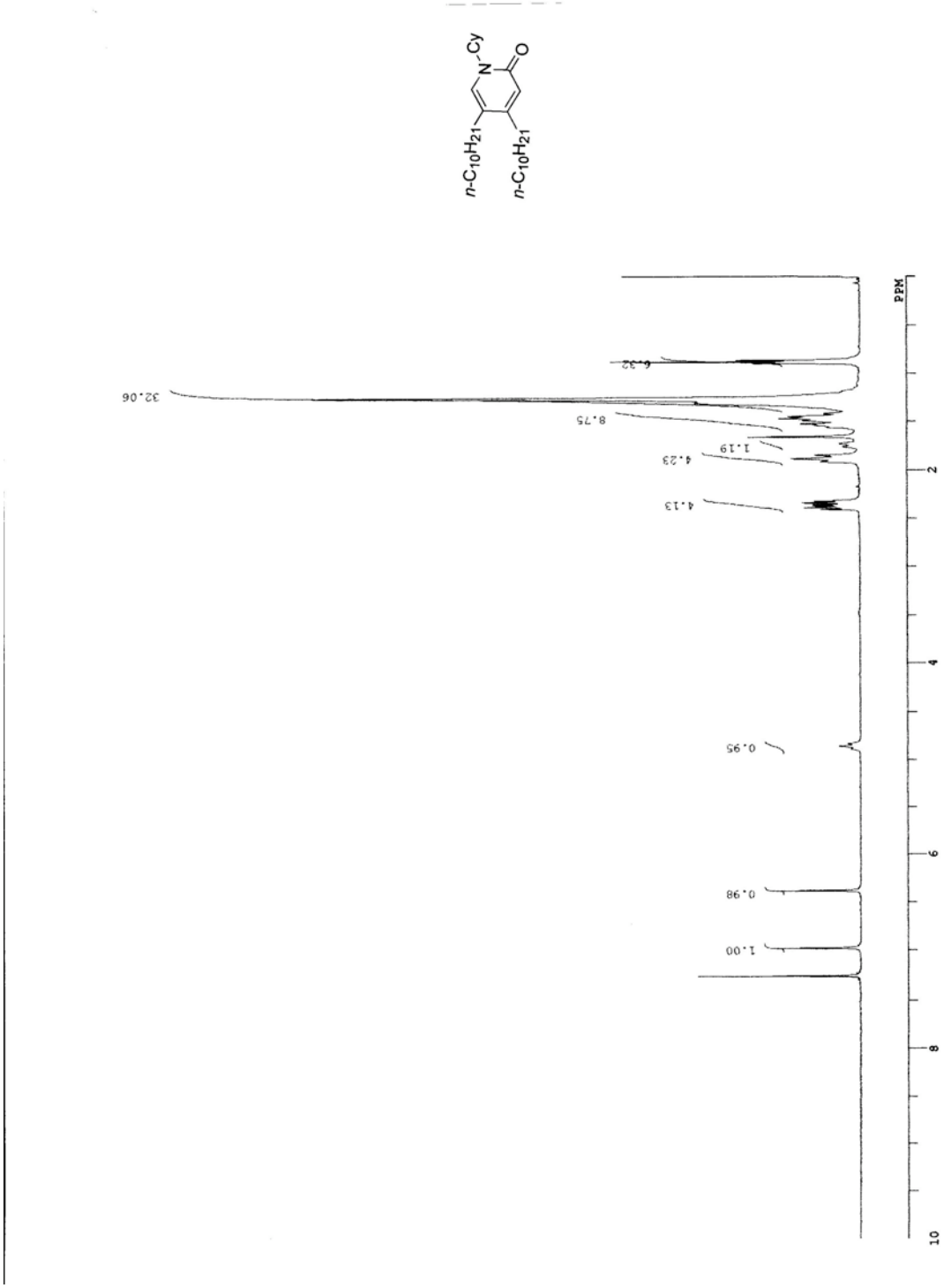
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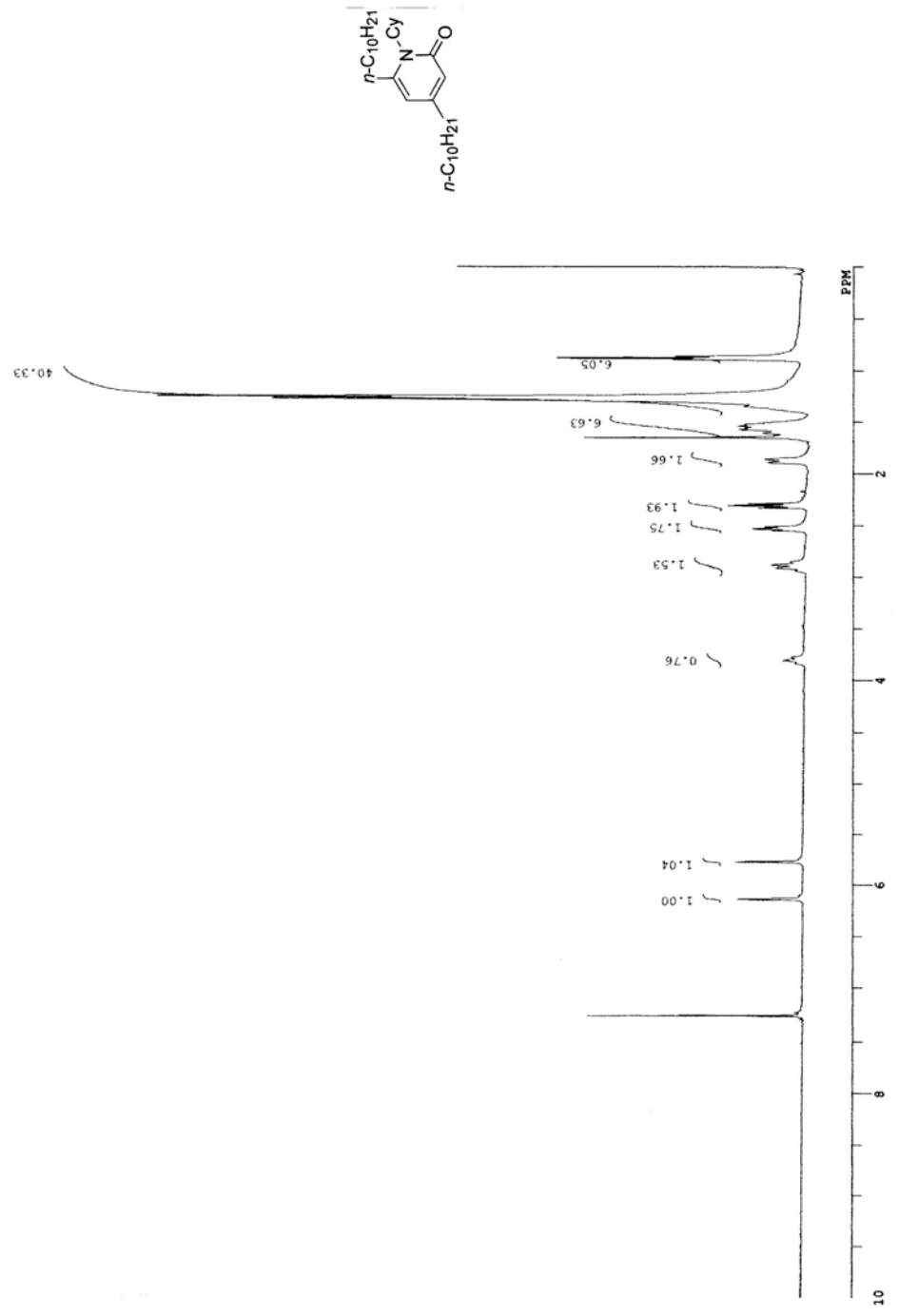
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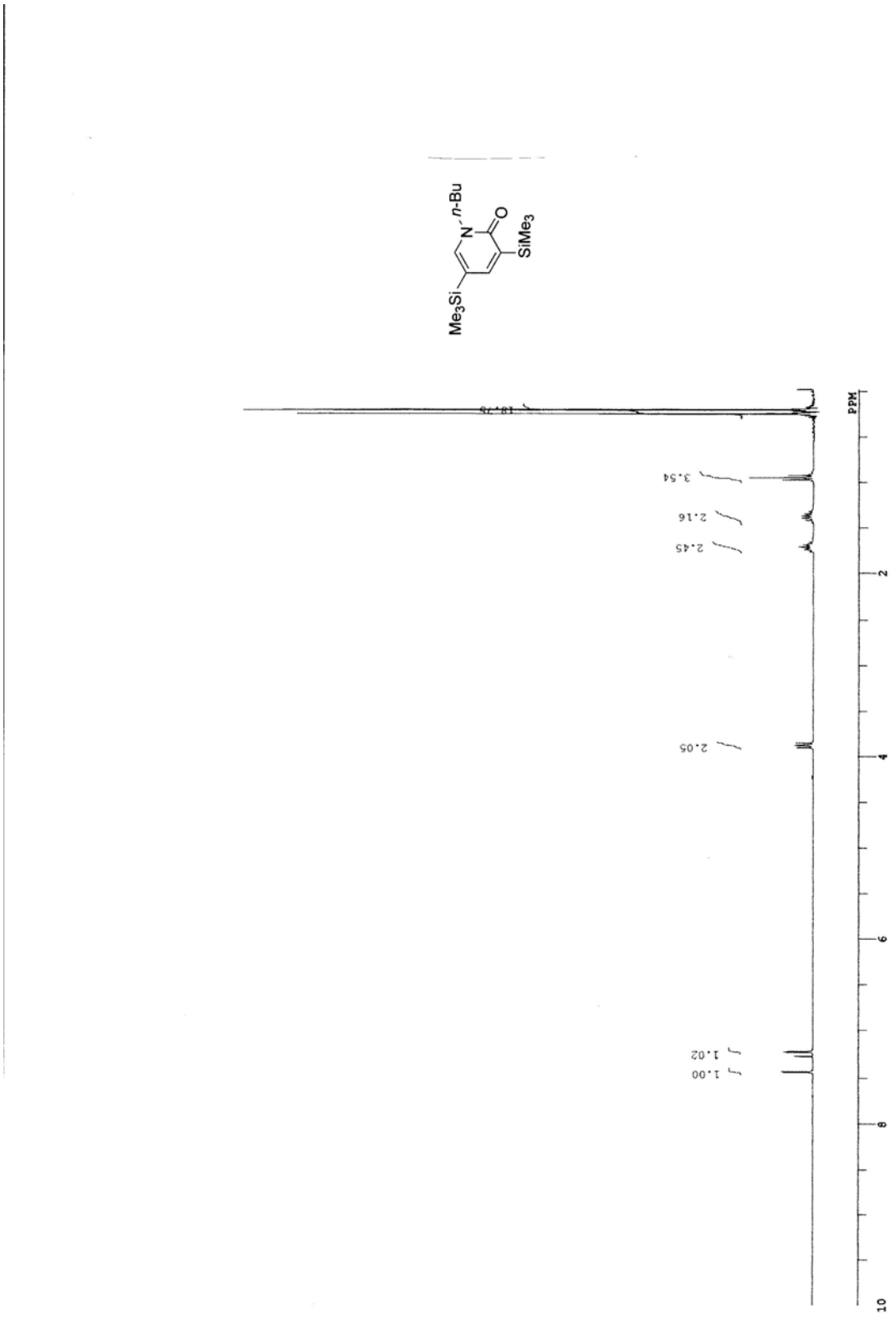
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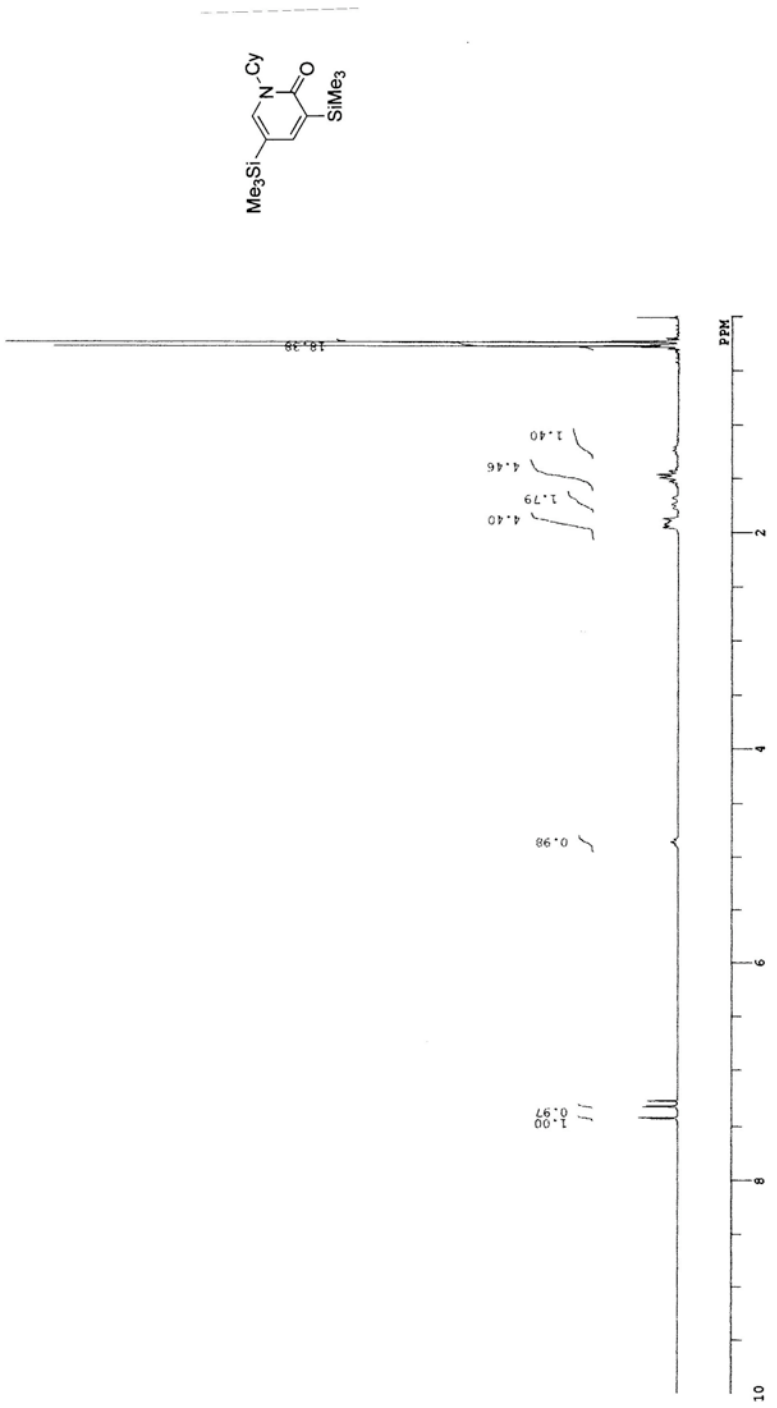
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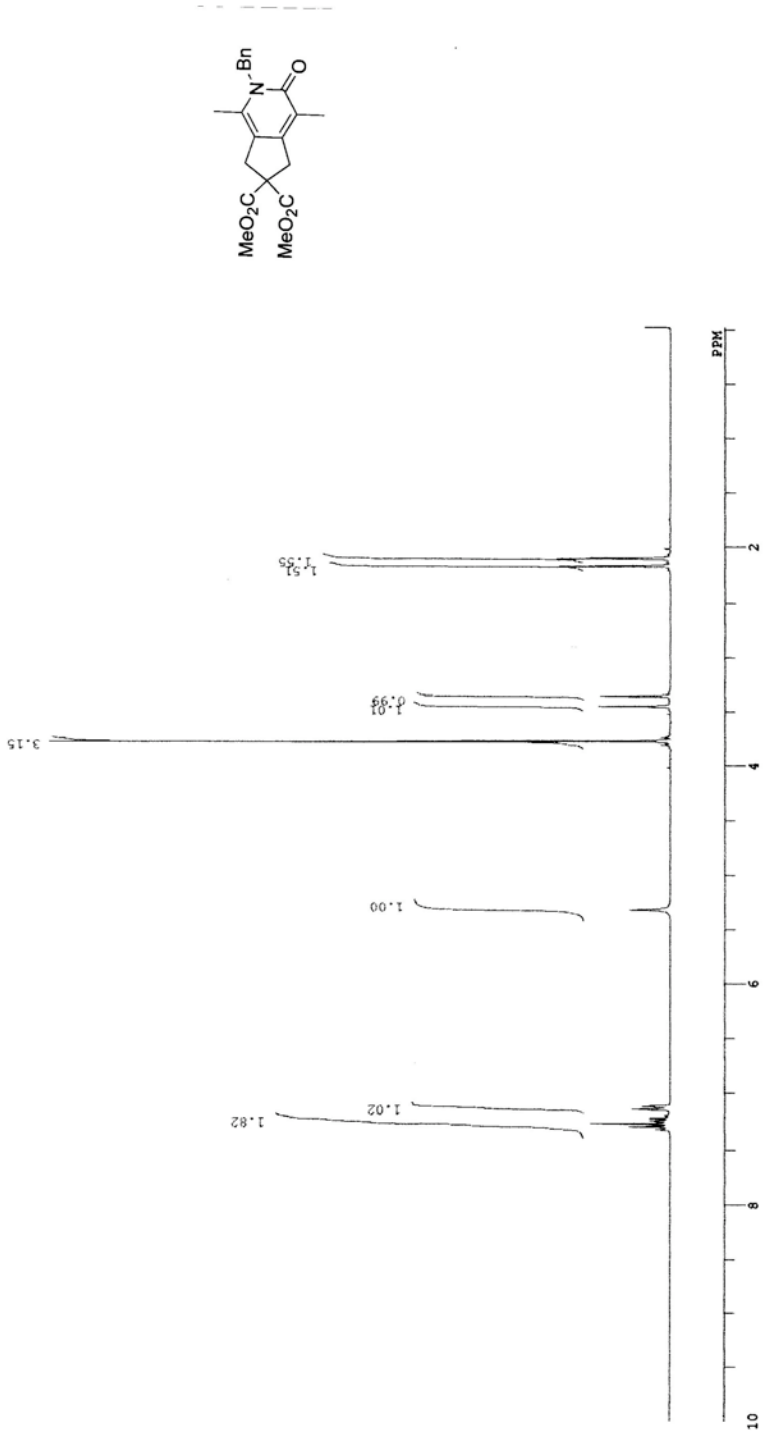
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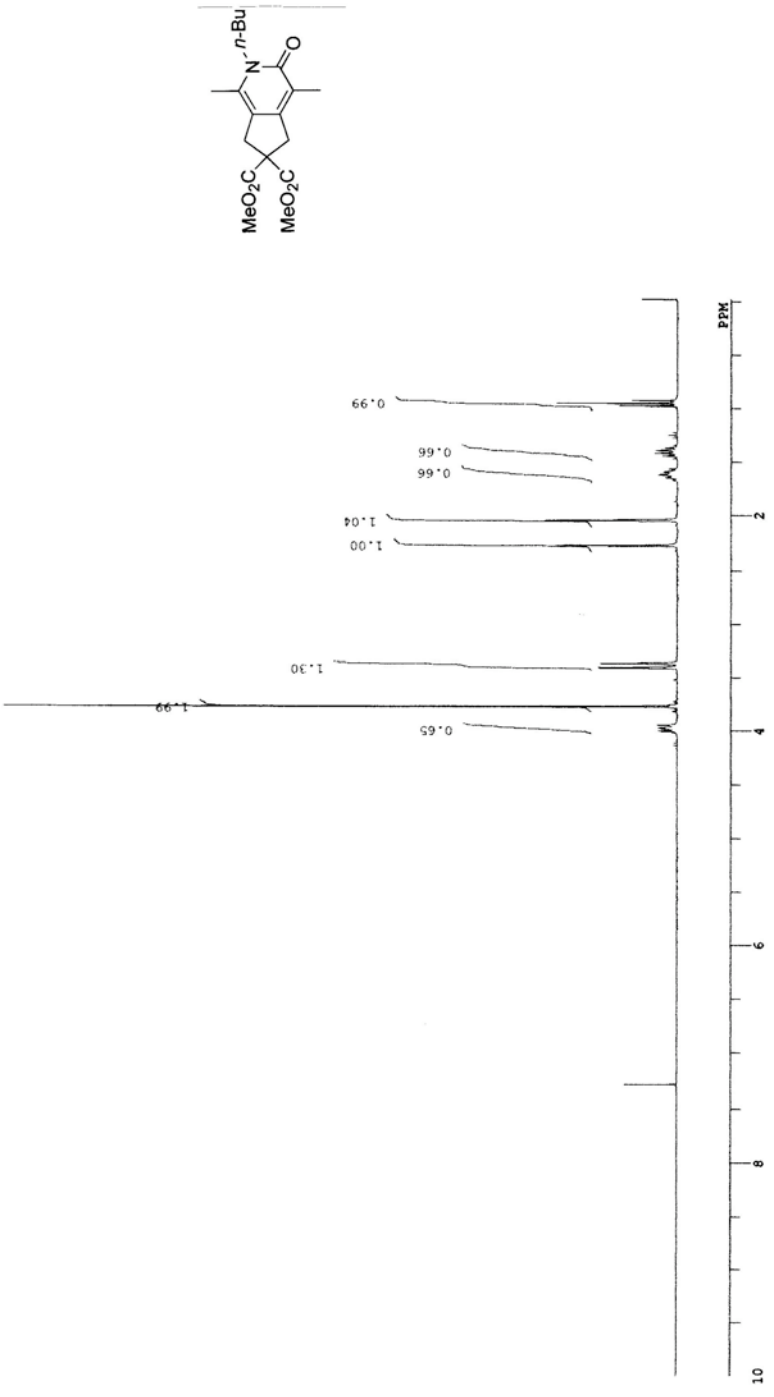
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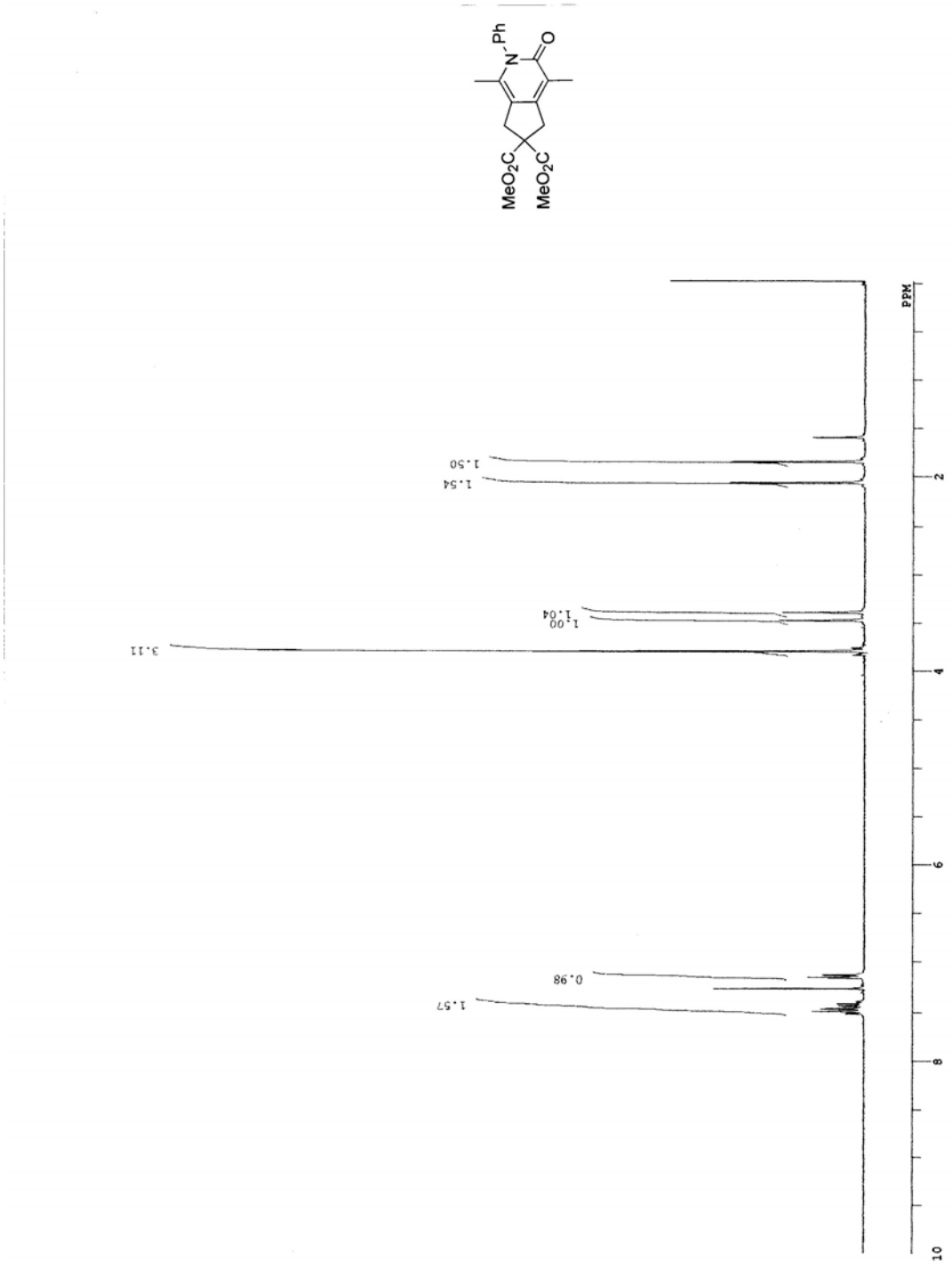
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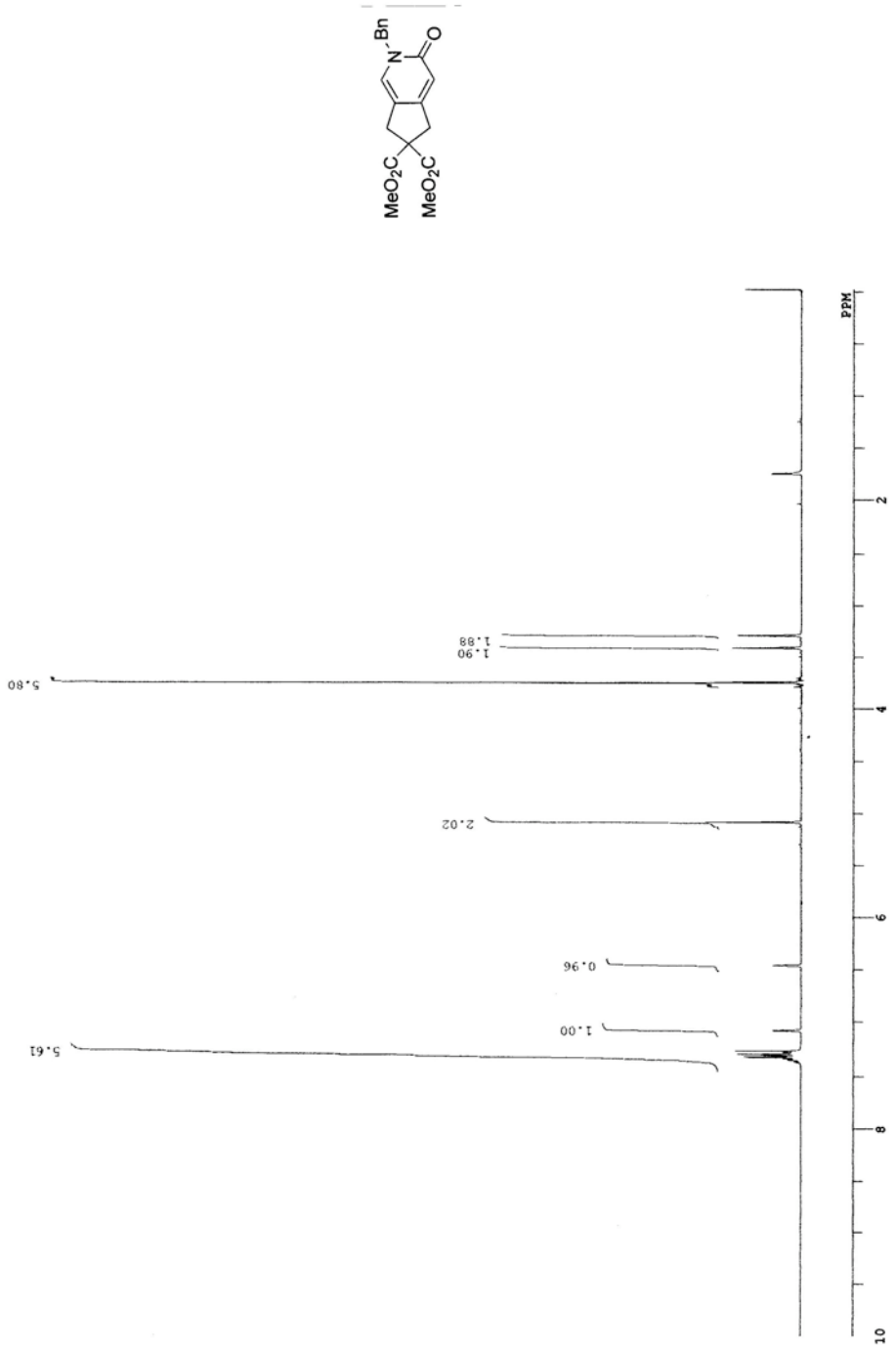
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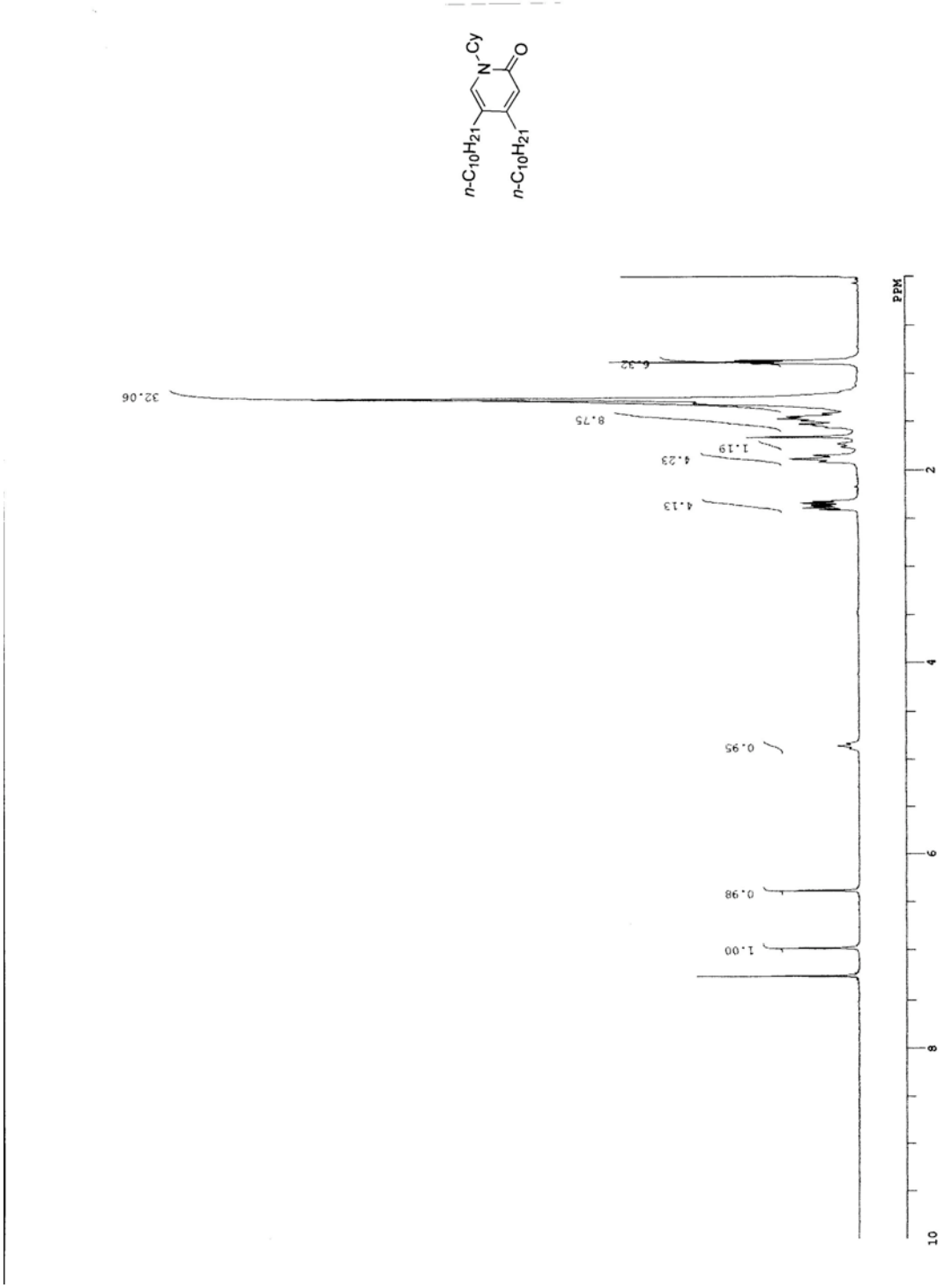
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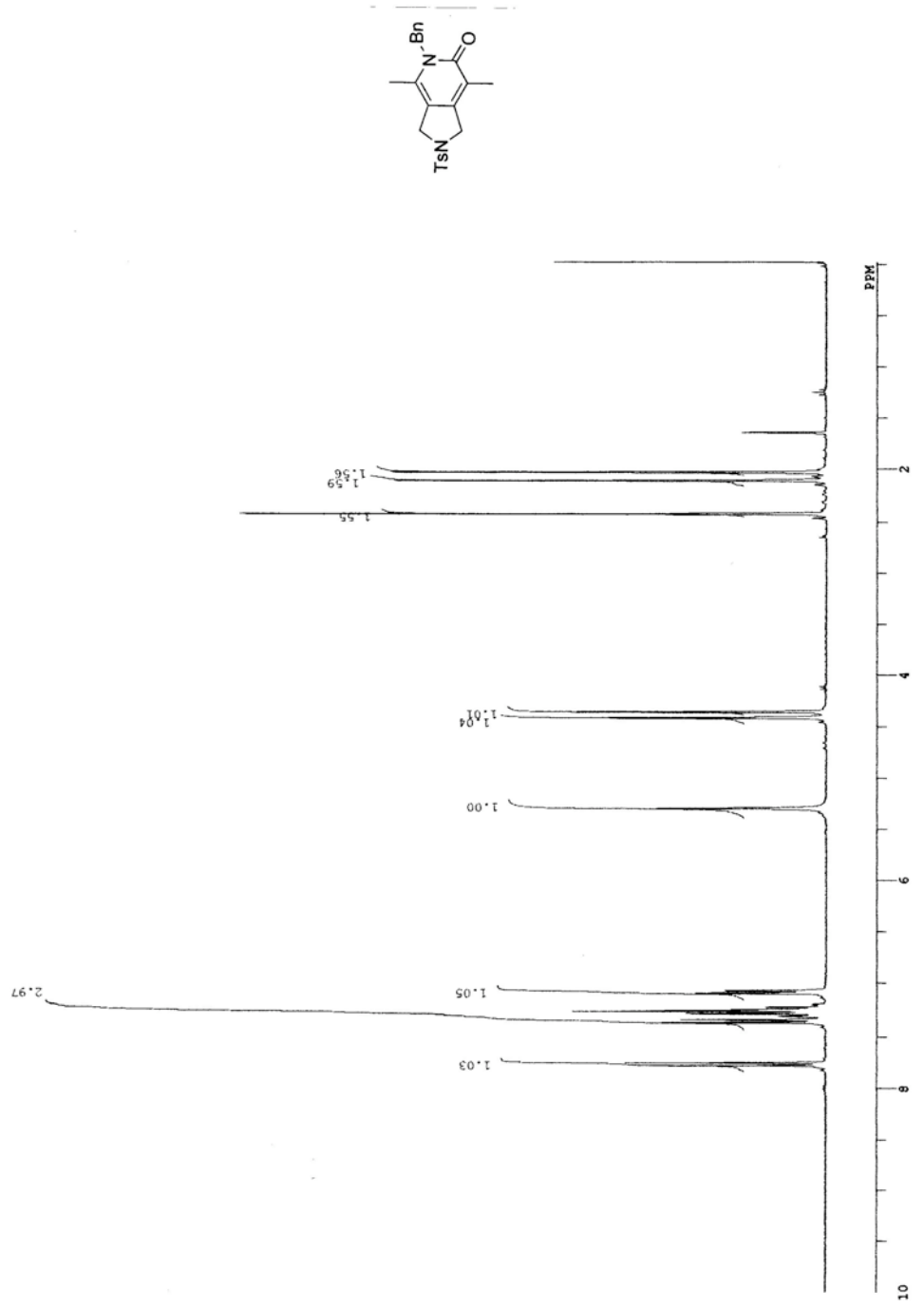
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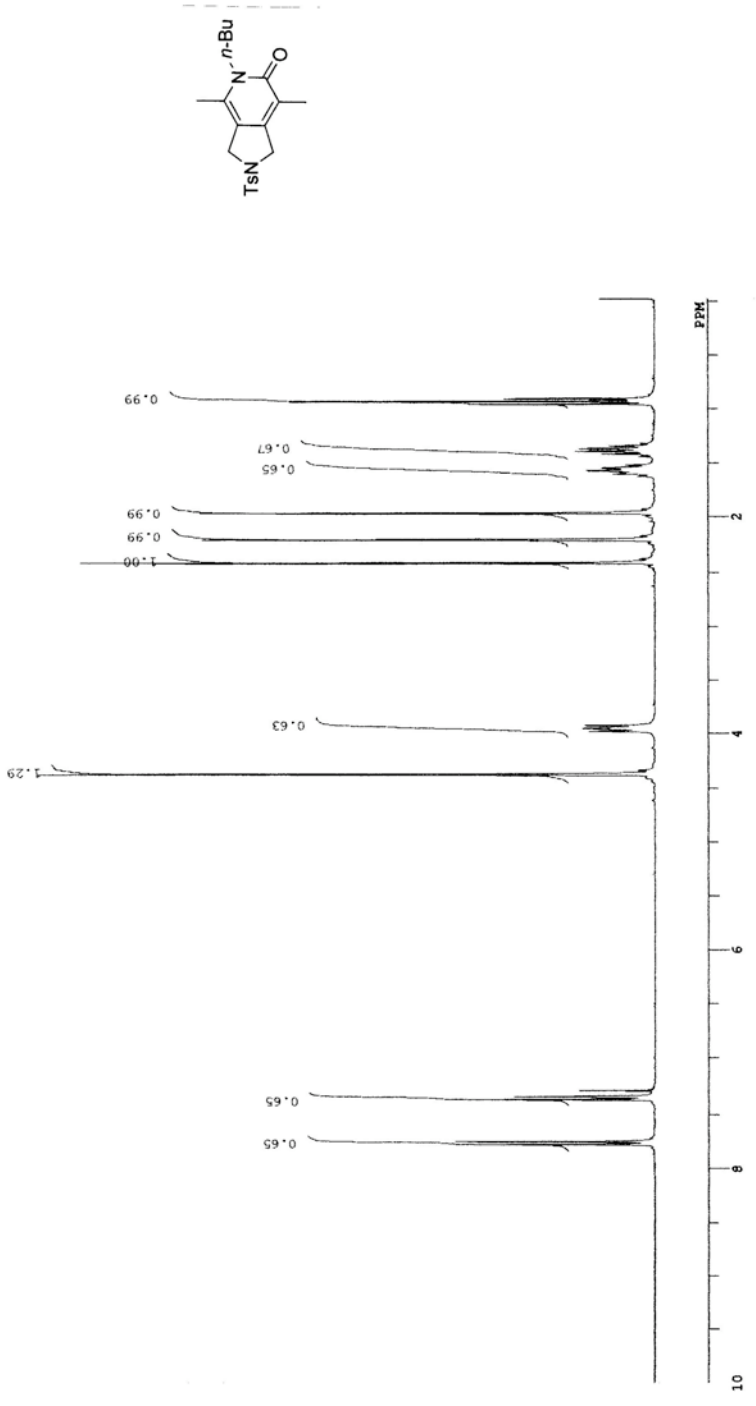
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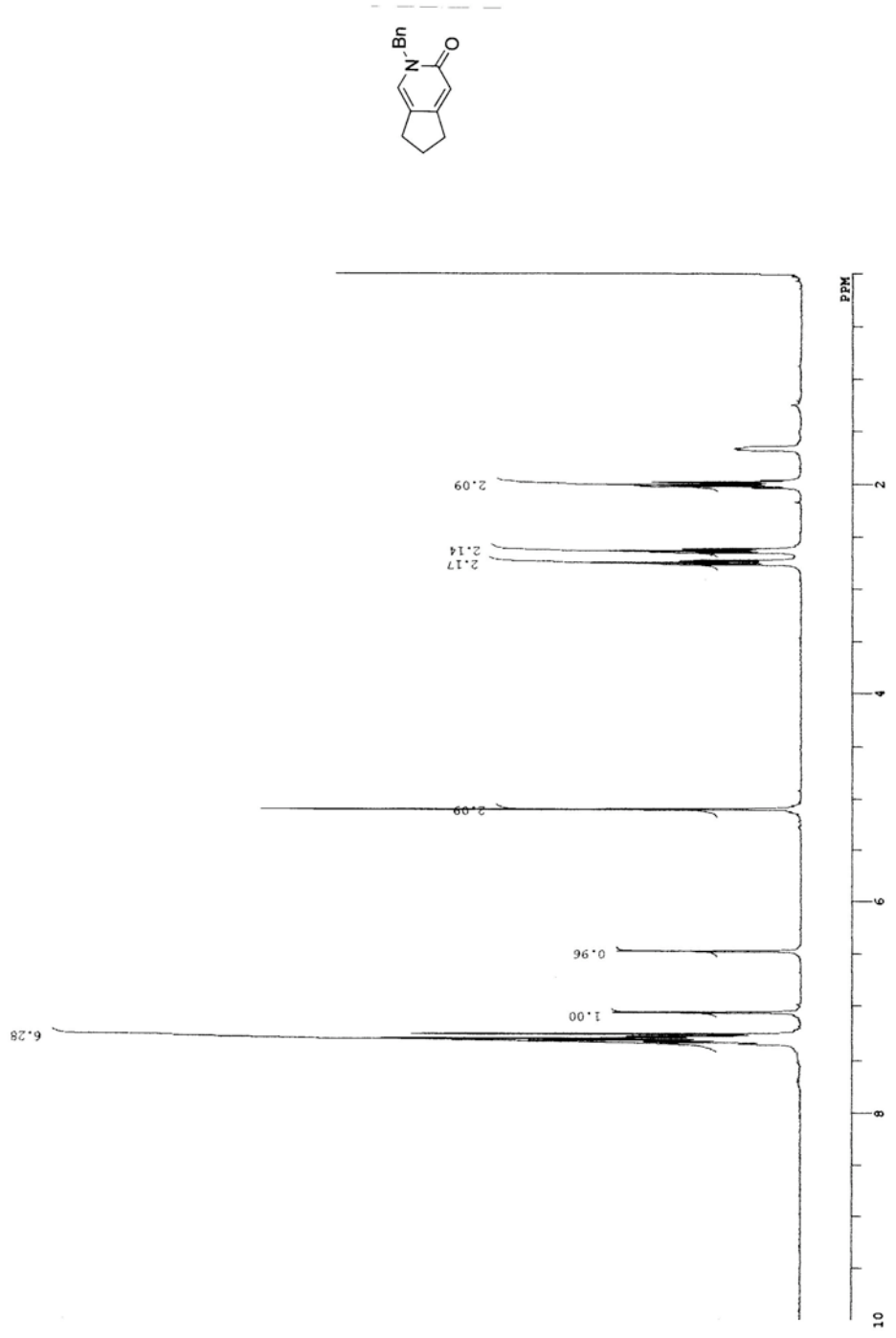
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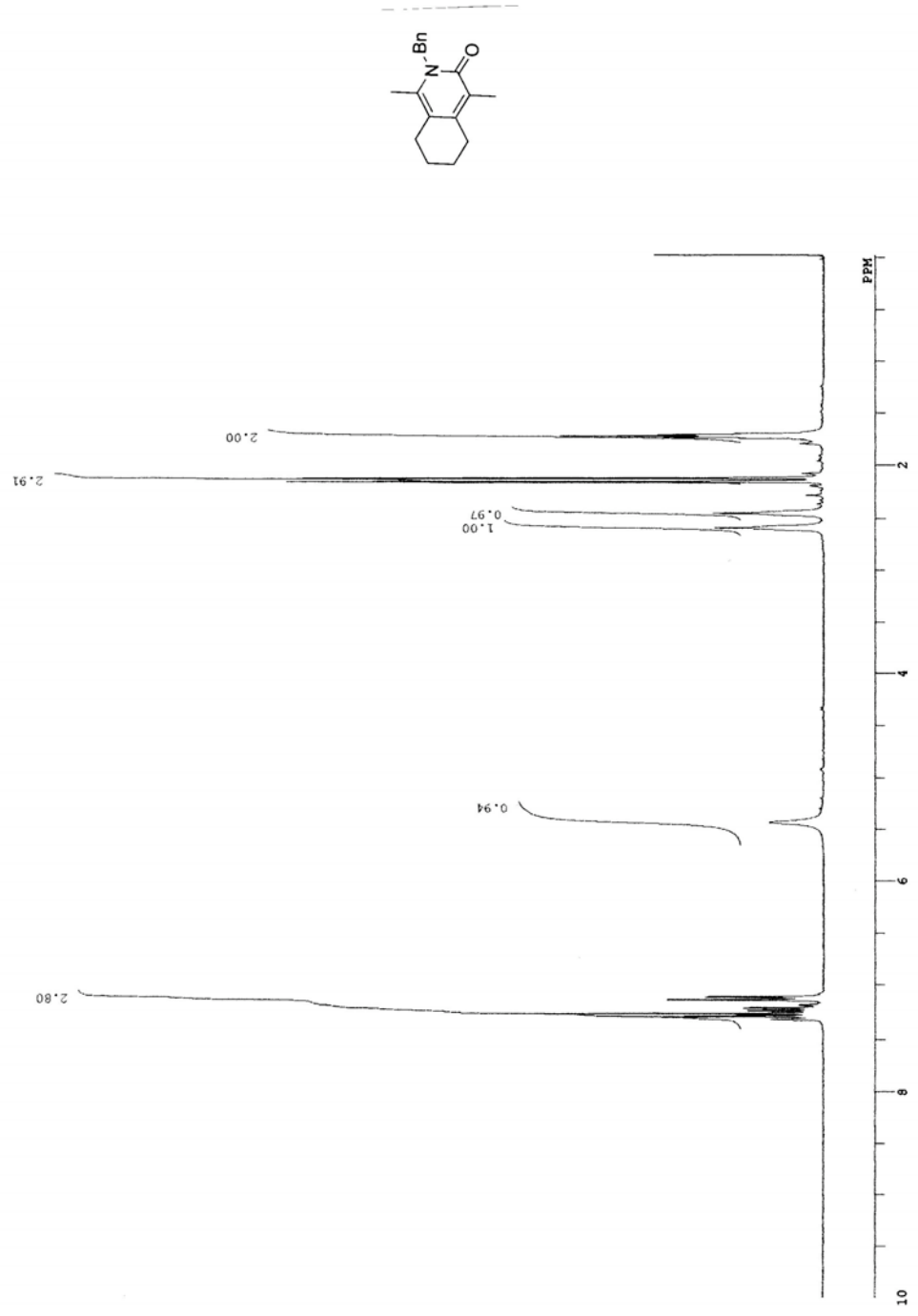
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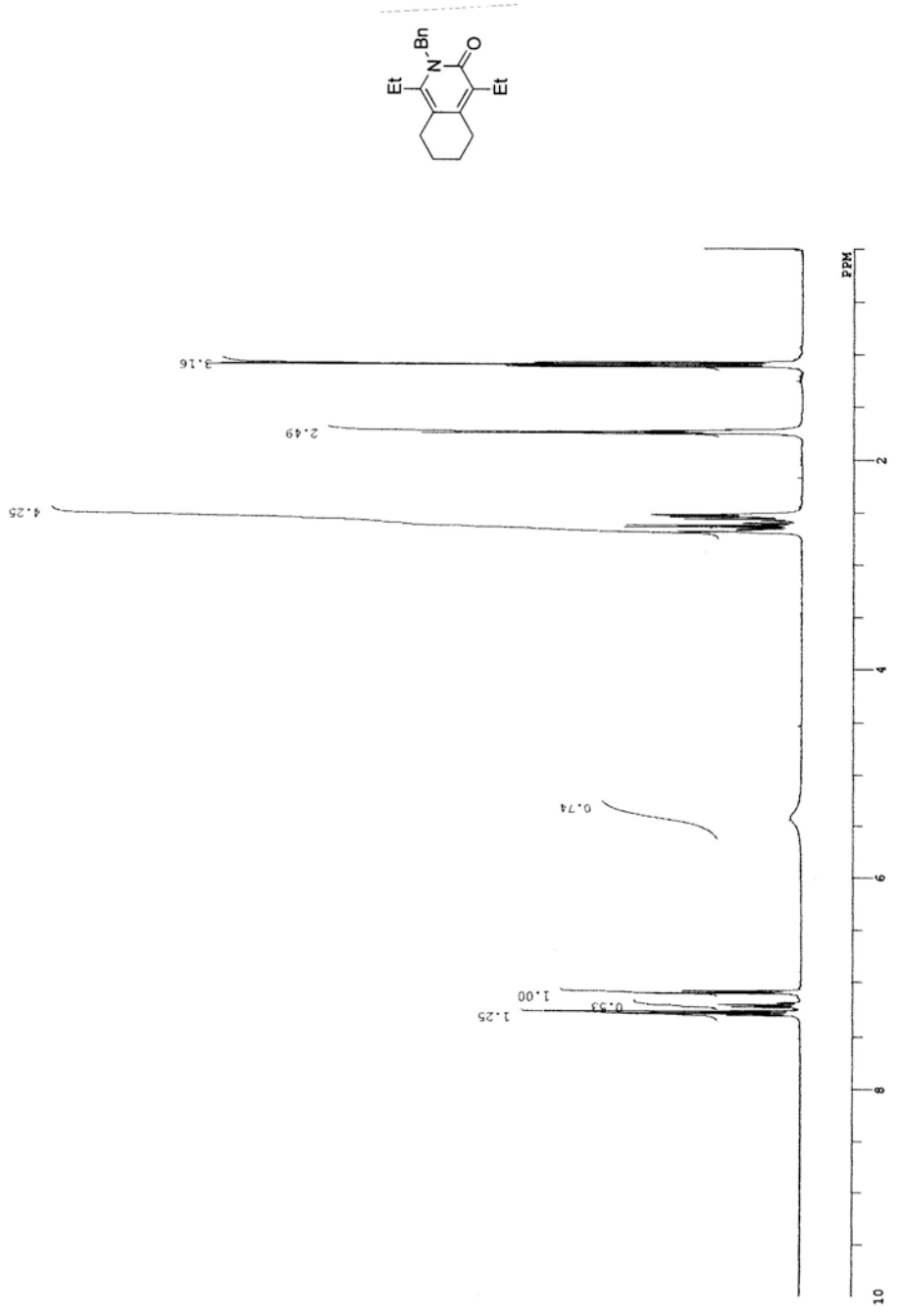
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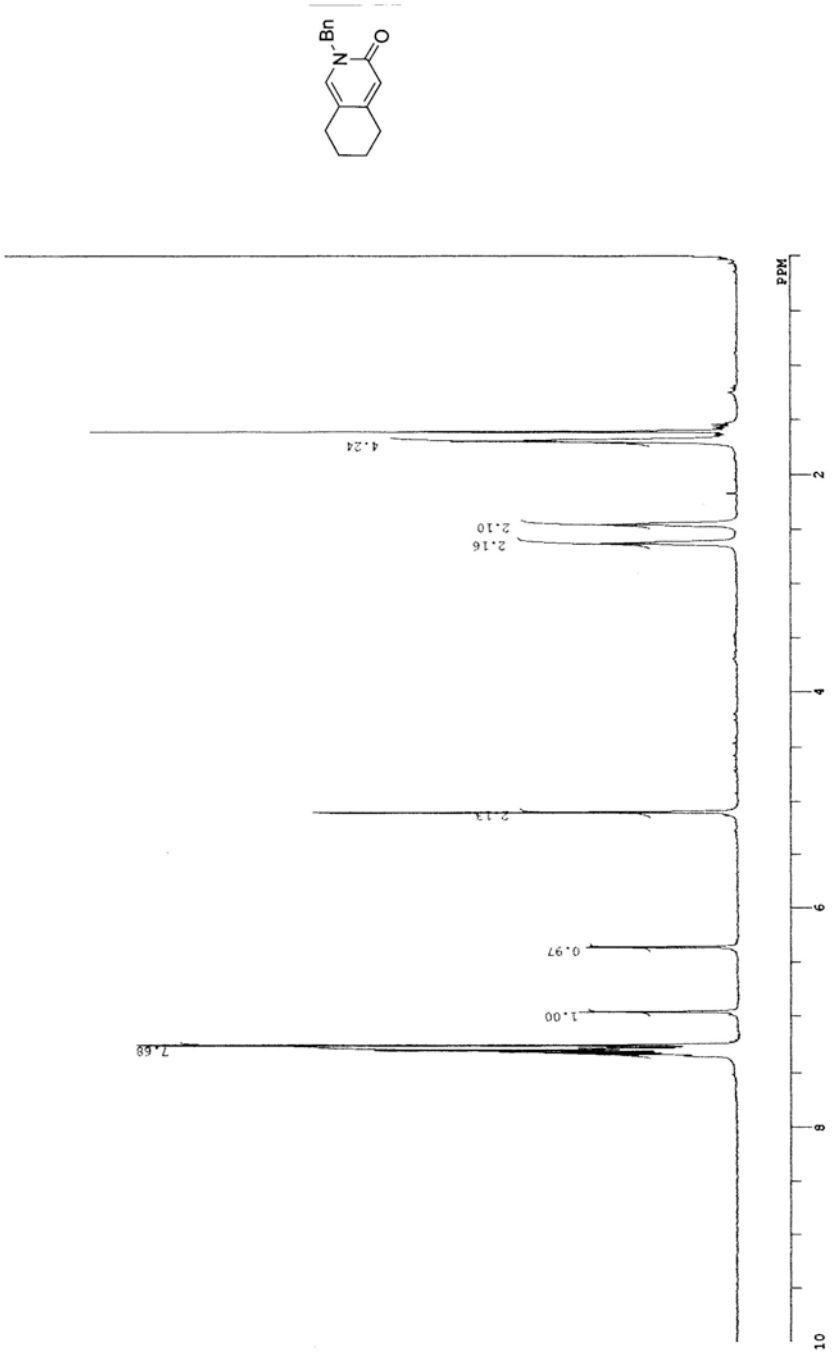
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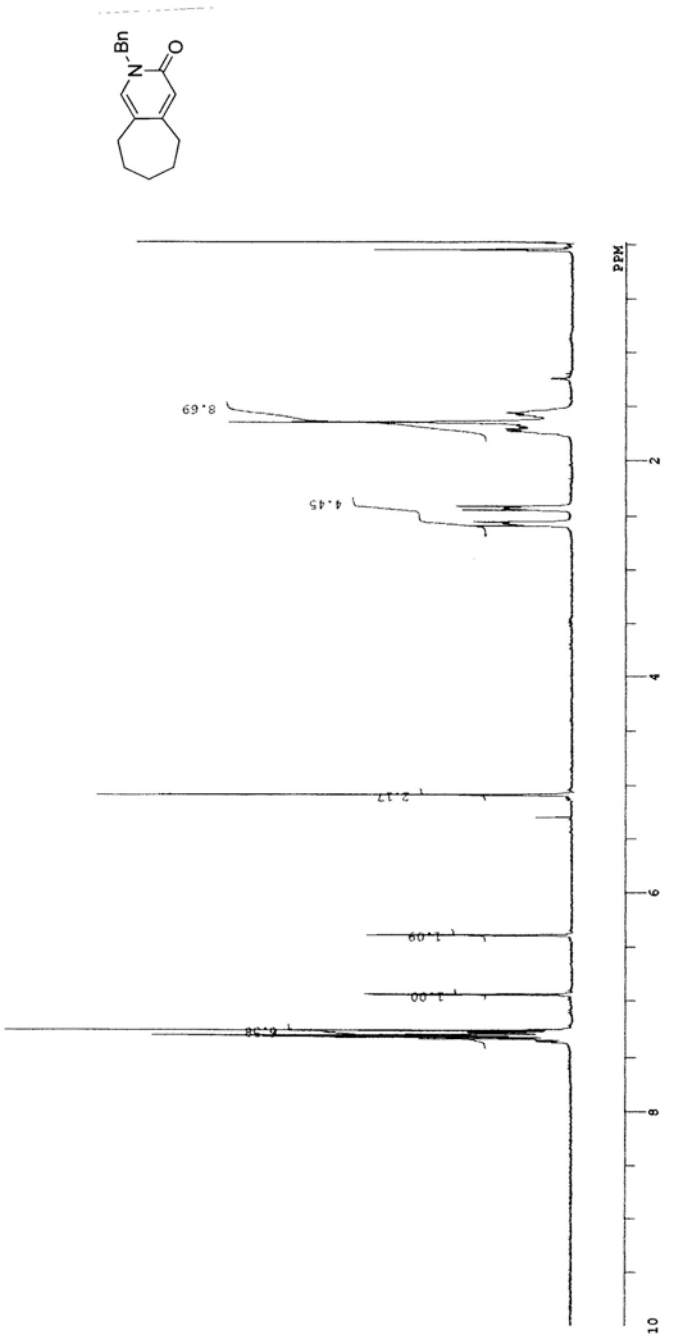
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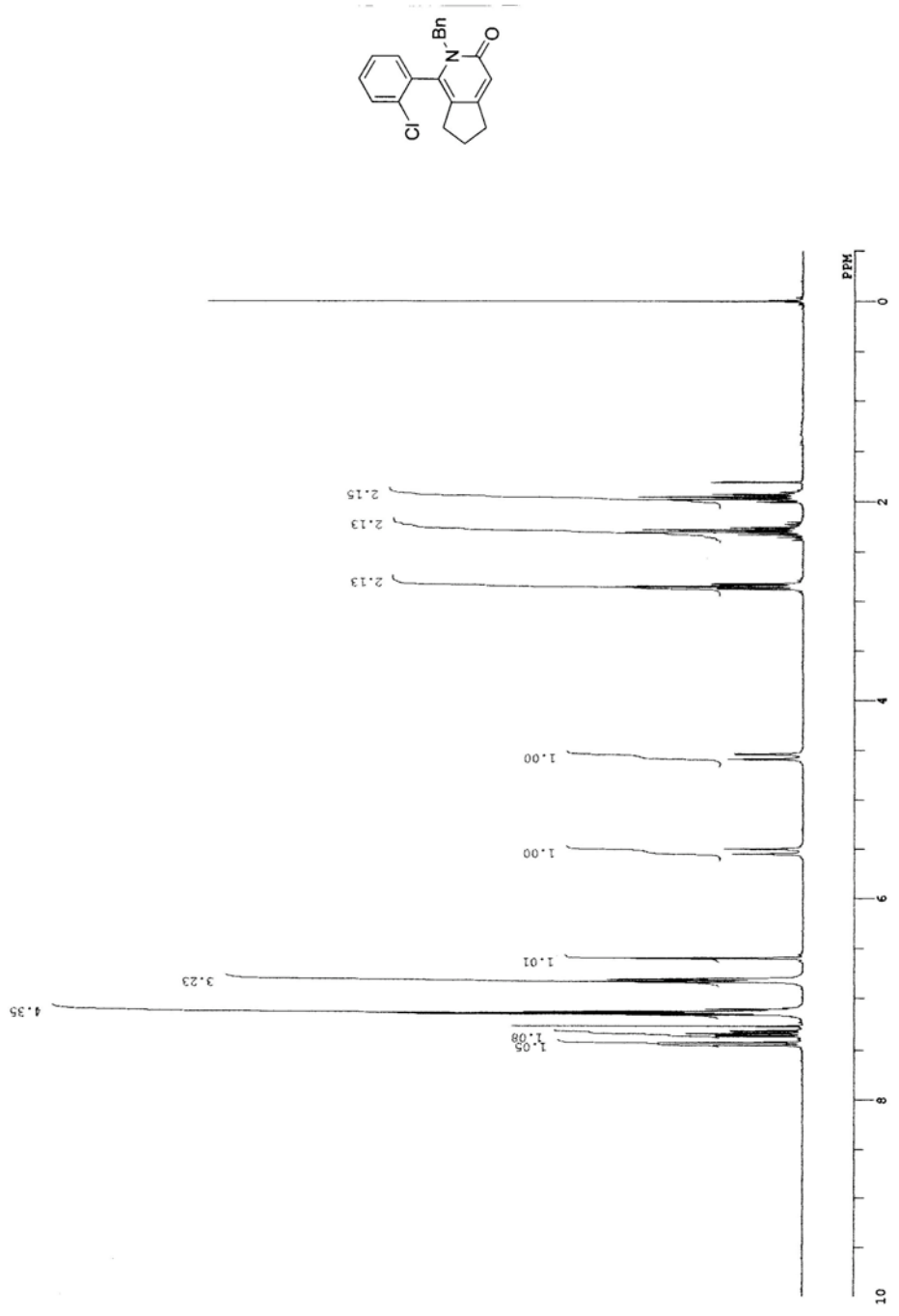
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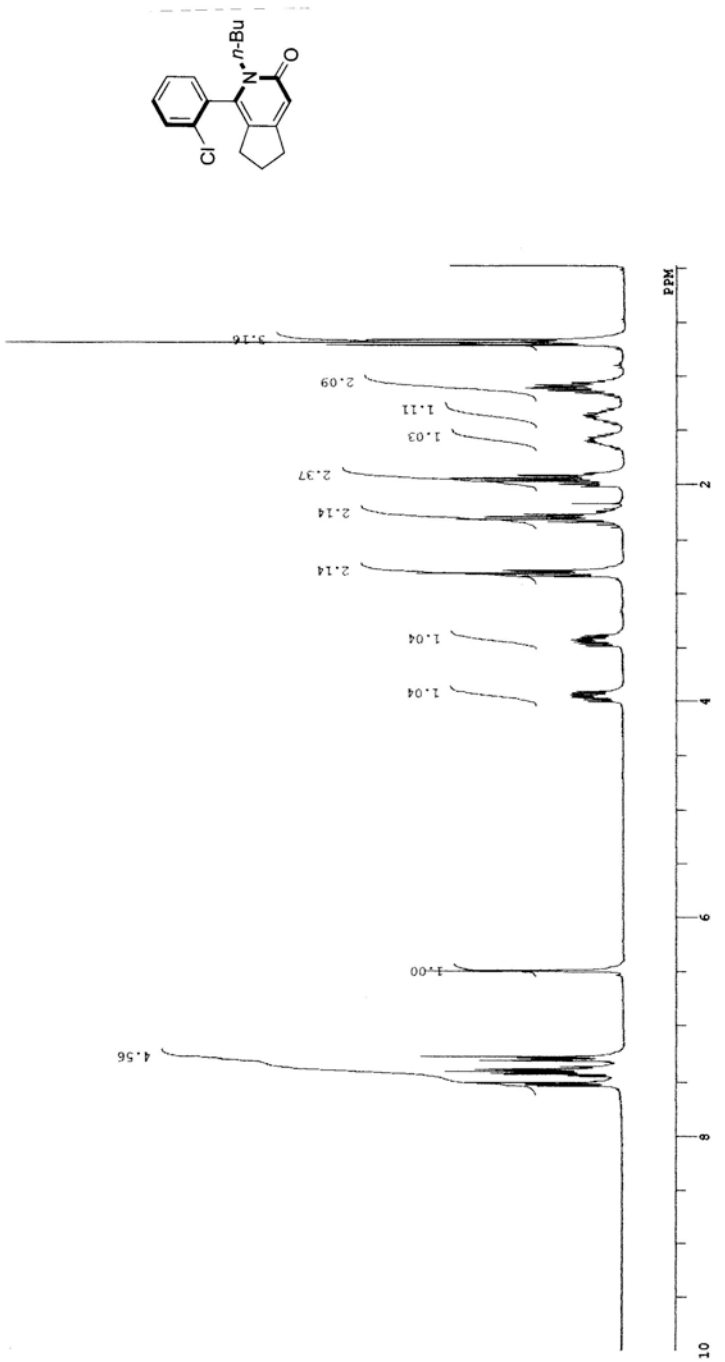
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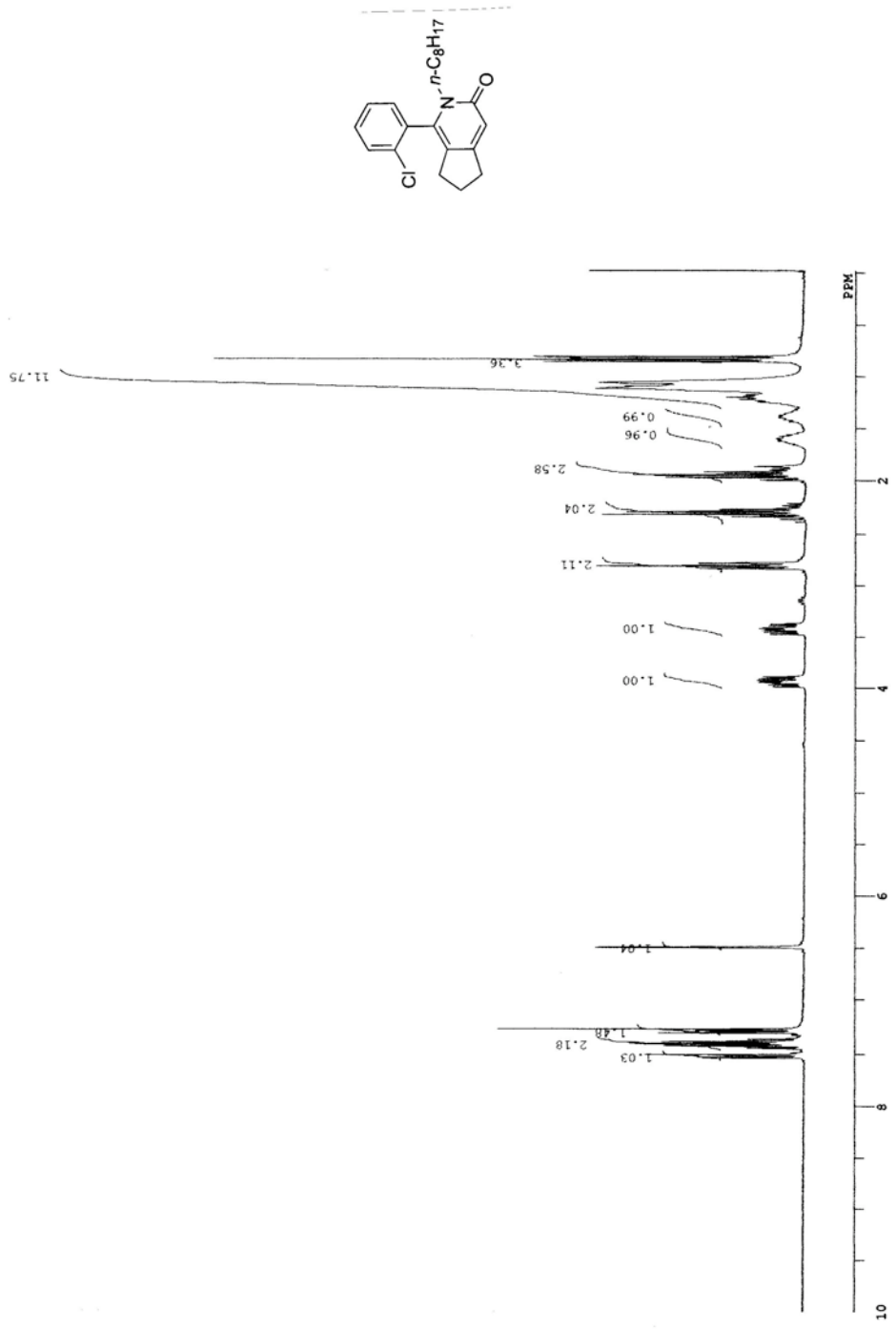
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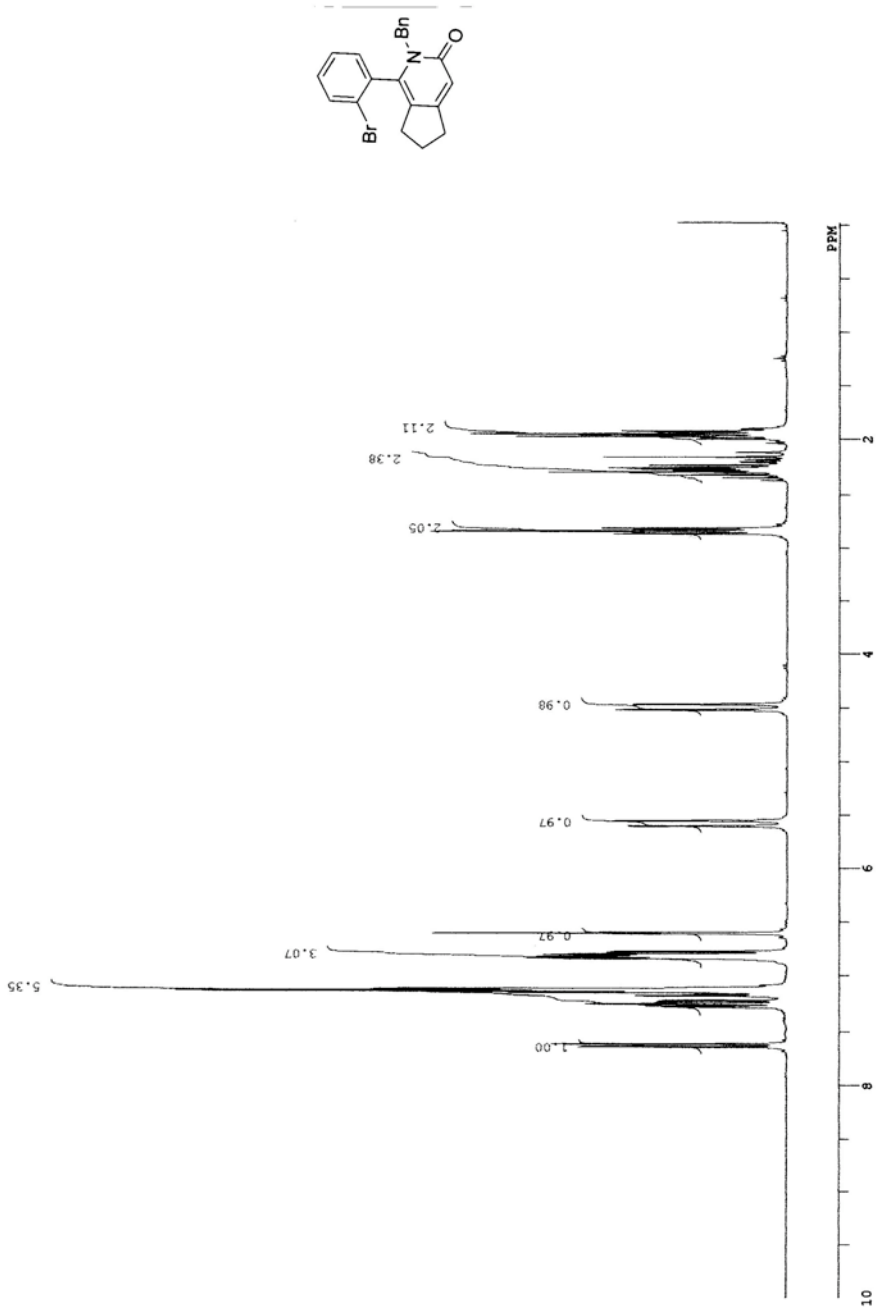
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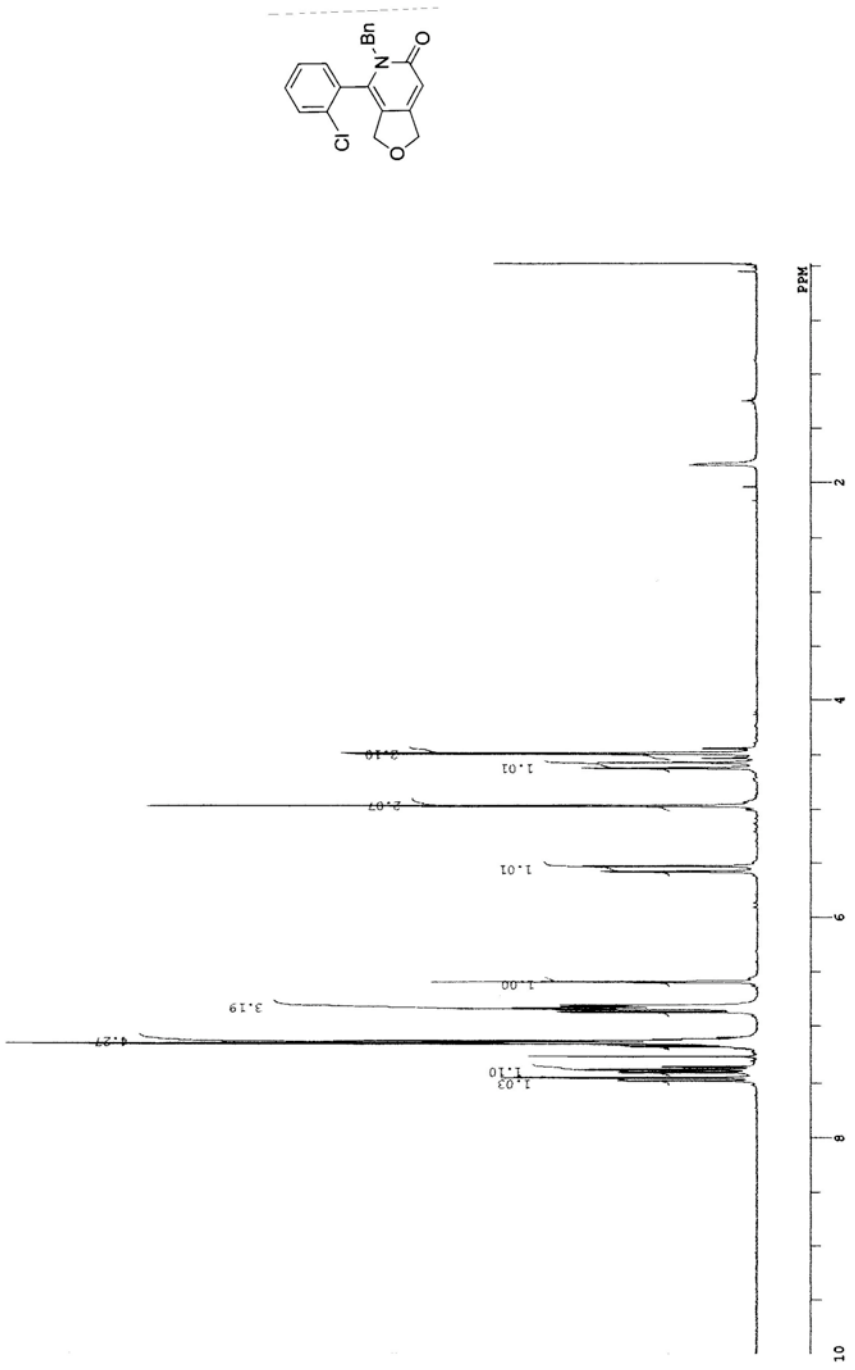
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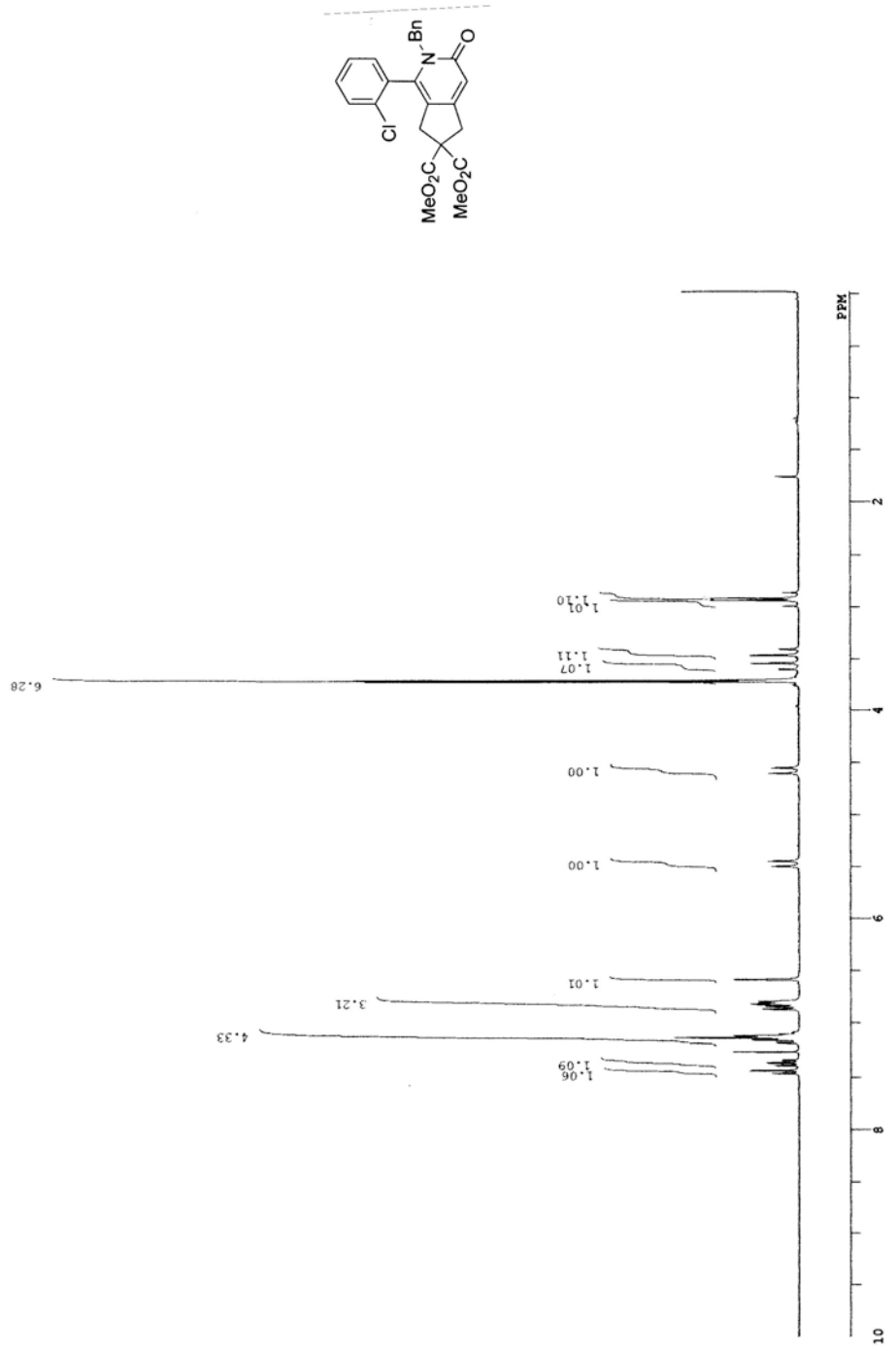
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