Supporting Information

Palladium-Catalyzed Benzylic Arylation of *N*-Benzylxanthone Imines

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Contents

Instrumentation and Chemicals

^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra were taken on a Varian Mercury 500 spectrometer in $CDCl_3$ [using tetramethylsilane (for ^{1}H, δ = 0.00 ppm) and $CDCl_3$ (for ^{13}C, δ = 77.2 ppm) as an internal standard] or DMSO-d_6 [using DMSO (for ^{1}H, δ = 2.50 ppm) and DMSO (for ^{13}C, δ = 39.7 ppm) as an internal standard]. IR spectra were determined on a SHIMADZU FTIR-8200PC spectrometer. TLC analyses were performed on commercial glass plates bearing a 0.25-mm layer of Merck Silica gel $60F_{254}$. Silica gel (Wakogel 200 mesh) was used for column chromatography. Elemental analyses were carried out at the Elemental Analysis Center of Kyoto University.

Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Toluene and xylene were purchased from Wako Pure Chemical Co. and stored over slices of sodium. Cesium hydroxide monohydrate was purchased from Nacalai Tesque. Tricyclohexylphosphine was purchased from Strem. Allylpalladium(II) chloride dimer was obtained from Aldrich Chemicals. All reactions were carried out under argon atmosphere. Preparations of xanthone imines (**1a**-**1f**) are shown below.

Experimental Procedure

Synthesis of *N*-Benzylxanthone imine (1a)

A solution of titanium(IV) chloride (4.1 mL, 37.5 mmol) in toluene (50 mL) was slowly added to a solution of xanthone (9.8 g, 50 mmol) and benzylamine (24.6 mL, 225 mmol) in toluene (150 mL) at 0 °C. The resulting mixture was stirred for 30 min at ambient temperture,

and then for 6 h at reflux. Diethyl ether (200 mL) was added, and the reaction mixture was passed through a pad of Celite with diethyl ether (40 mL × 3). The solvent was removed under reduced pressure. *N*-Benzylxanthone imine (**1a**) was recrystallized from hexane/toluene as a white solid (13.1 g, 46 mmol) in 92% yield.

Procedure for Palladium-catalyzed Direct Arylation of *N*-Benzylxanthone imine (1a)

Cesium hydroxide monohydrate (0.18 g, 1.05 mmol) and allylpalladium chloride dimer (9.1 mg, 0.025 mmol) were placed in a 20-mL two-necked reaction flask equipped with a Dimroth condenser under Ar atmosphere. Tricyclohexylphosphine (0.5 M in toluene, 0.40 mL, 0.20 mmol), xylene (2.0 mL), *N*-benzylxanthone imine (**1a**) (285 mg, 1.0 mmol), and chlorobenzene (0.12 mL, 1.2 mmol) were sequentially added at ambient temperature. The resulting mixture was heated at reflux for 24 h. After the mixture was cooled to room temperature, a saturated aqueous ammonium chloride solution (5 mL) was added. The product was extracted with chloroform (10 mL × 3). The combined organic layer was dried over sodium sulfate, and concentrated in vacuo. The residue included a mixture of imines **2a** and **2a'** (7 : 3), which was used for the next step without further purification.

Typical Procedure for Preparation of Benzhydrylamines (3a–3e, 3g–3j) by Reduction with Sodium Cyanoborohydride and Hydrochloric Acid

Reduction of a mixture of **2a** and **2a'** is representative. A drop of hydrochloric acid (12 M) was added to a solution of the crude mixture of **2a** and **2a'** and sodium cyanoborohydride (189 mg, 3.0 mmol) in ethanol (5 mL). The resulting mixture was stirred at 25 ˚C for 2 h. Hydrochloric acid (12 M, 5 mL) and water (1 mL) were then added, and the resulting mixture was stirred at 25 ˚C for 2 h. The reaction was quenched with water (10 mL), and diethyl ether (10 mL) was then added. The product was extracted with hydrochloric acid (1 M, 5 mL × 3). The combined aqueous layer was neutralized with sodium hydroxide, and extracted with chloroform (5 mL × 3). The combined organic layer was dried over sodium sulfate, and concentrated in vacuo. The residue containing amine **3a** was used for the next step without further purification.

Preparation of Benzhydrylamine 3f by Reduction with Sodium Cyanoborohydride and Formic Acid

A drop of formic acid was added to a solution of the crude mixture of **2f** and **2f'** and sodium cyanoborohydride (189 mg, 3.0 mmol) in ethanol (5 mL). The resulting mixture was stirred at 80 ˚C for 2 h. Formic acid (12 M, 5 mL) and water (1 mL) were then added, and the

resulting mixture was stirred at 80 ˚C for 2 h. The reaction was quenched with water (10 mL), and diethyl ether (10 mL) was then added. The product was extracted with hydrochloric acid (1 M, 5 mL × 3). The combined aqueous layer was neutralized with sodium hydroxide, and extracted with chloroform (5 mL × 3). The combined organic layer was dried over sodium sulfate, and concentrated in vacuo. The residue containing amine **3f** was used for the next step without further purification.

Isolation of Benzhydrylamine Hydrochloride (3a•HCl)

Hydrochloride in ether (1.0 M, 2.0 mL, 2.0 mmol) was added to a solution of the crude amine **3a** in methanol (5 mL). After the mixture was stirred for 2 h at room temperature, the solvent was removed in vacuo. Anhydrous ether (20 mL) was added to the resulting mixture. Insoluble materials were collected by filtration to yield benzhydrylamine hydrochloride (**3a•HCl**) (183 mg, 0.83 mmol, 83% overall yield).

Typical Procedure for Benzoylation of Benzhydrylamines

Benzoylation of the crude amine **3f** is representative. Benzoyl chloride (0.12 mL, 1.0 mmol) was added to a solution of the crude amine **3f** and triethylamine (0.28 mL, 2.0 mmol) in dichloromethane (5 mL). After the mixture was stirred for 2 h at room temperature, the reaction was quenched with water (10 mL). The product was extracted with chloroform (5 mL × 3). The combined organic layer was dried over sodium sulfate, and concentrated in vacuo. Silica gel column purification (hexane/ethyl acetate = 5 : 1) provided *N*-benzhydrylbenzamide **3f•Bz** (146 mg, 0.47 mmol) in 47% overall yield.

Procedure for Suzuki-Miyaura Cross-Coupling Reaction of Imine 1f with Arylboronic acid 7

Sodium hydroxide (30 mg, 0.75 mmol), tetrakis(triphenylphosphine)palladium (11.6 mg, 0.01 mmol), arylboronic acid **7** (152 mg, 1.0 mmol), and imine **1f** (182 mg, 0.50 mmol) were placed in a 20-mL two-necked reaction flask equipped with a Dimroth condenser under Ar atmosphere. Dimethoxyethane (3.0 mL) and water (0.5 mL) were sequentially added at ambient temperature. The resulting mixture was heated at 100 ˚C for 24 h. After the mixture was cooled to room temperature, a saturated aqueous ammonium chloride solution (5 mL) was added. The product was extracted with ethyl acetate (10 mL × 3). The combined organic layer was dried over sodium sulfate, and concentrated in vacuo. Chromatographic purification through a short silica gel column (hexane/ethyl acetate = 1 : 1) provided crude product. The yield of the product **8** (60%) was determined by ^{1}H NMR measurement with 1,1,2,2-tetrachloroethane as an

internal standard. The residue was used for the next step without further purification.

Procedure for Intramolecular Benzylic Arylation of Imine 8

Cesium hydroxide monohydrate (0.88 g, 0.53 mmol) and allylpalladium chloride dimer (4.6 mg, 0.013 mmol) were placed in a 20-mL two-necked reaction flask equipped with a Dimroth condenser under Ar atmosphere. Tricyclohexylphosphine (0.5 M in toluene, 0.2 ml, 0.10 mmol), xylene (2.5 mL), and imine **8** were sequentially added at ambient temperature. The resulting mixture was heated at reflux for 24 h. After the mixture was cooled to room temperature, a saturated aqueous ammonium chloride solution (5 mL) was added. The product was extracted with chloroform (10 mL × 3). The combined organic layer was dried over sodium sulfate, and concentrated in vacuo. The residue was used for the next step without further purification.

Preparation of 9-Fluorenylamine by Reduction with Sodium Cyanoborohydride and Hydrochloric Acid

A drop of hydrochloric acid (12 M) was added to a solution of the crude imine **8** and sodium cyanoborohydride (90 mg, 1.5 mmol) in ethanol (2.5 mL). The resulting mixture was stirred at 25 ˚C for 2 h. Hydrochloric acid (12 M, 2.5 mL) and water (0.5 mL) were then added, and the resulting mixture was stirred at 25 ˚C for 2 h. The reaction was quenched with water (5 mL), and diethyl ether (5 mL) was then added. The product was extracted with hydrochloric acid (1 M, 3 mL × 3). The combined aqueous layer was neutralized with sodium hydroxide, and extracted with chloroform (5 mL × 3). The combined organic layer was dried over sodium sulfate, and concentrated in vacuo. The residue containing 9-fluorenylamine (**9**) was used for the next step without further purification.

Isolation of *N*-(9-Fluorenyl)acetamide (9)

Acetyl chloride (0.11 mL, 1.5 mmol) was added to a solution of the crude amine and triethylamine (0.21 mL, 1.5 mmol) in dichloromethane (5 mL). After the mixture was stirred for 2 h at room temperature, the reaction was quenched with water (10 mL). The product was extracted with chloroform (5 mL × 3). The combined organic layer was dried over sodium sulfate, and concentrated in vacuo. Silica gel column purification (hexane/ethyl acetate = 5 : 1) provided *N*-(9-fluorenyl)acetamide (**9**, 47 mg, 0.21 mmol) in 70% isolated yield starting from **8**.

Characterization Data

***N*-Benzylxanthone Imine (1a)**: IR (nujol) 1602, 1247, 1124, 753 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.25 (s, 2H), 7.20–7.29 (m, 4H), 7.37–7.41 (m, 3H), 7.46 (ddd, *J* = 7.0, 1.5, 1.5 Hz, 1H), 7.50–7.52 (m, 3H), 7.96 (dd, *J* = 7.0, 1.5 Hz, 1H), 8.31 (dd, *J* = 7.0, 1.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 56.7, 116.5, 118.4, 118.9, 122.4, 123.8, 126.0, 126.6, 127.4, 127.4, 128.4, 128.4, 128.8, 130.9, 131.6, 141.6, 152.7, 155.0. Found: C, 84.46; H, 5.32; N, 4.84%. Calcd for $C_{20}H_{15}NO$: C, 84.19; H, 5.30; N, 4.91%. m.p.: 98–100 ˚C.

***N*-(4-Methylphenylmethyl)xanthone Imine (1b)**: IR (nujol) 1609, 1558, 1507, 1457, 1249, 754 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.36 (s, 3H), 5.20 (s, 2H), 7.18–7.25 (m, 5H), 7.37–7.40 (m, 3H), 7.44 (ddd, *J* = 8.0, 8.0, 1.5Hz, 1H), 7.49 (ddd, *J* = 8.0, 8.0, 1.5 Hz, 1H), 7.94 (dd, *J* = 8.0, 1.5 Hz, 1H), 8.30 (dd, *J* = 7.5, 1.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 21.3, 56.6, 116.7, 118.5, 119.1, 122.5, 124.0, 125.2, 126.2, 127.5, 129.0, 129.3, 131.1, 131.7, 136.3, 138.7, 150.9, 152.9, 155.1. m.p.: 118–121 ˚C.

***N*-(1-Naphthylmethyl)xanthone Imine (1c)**: IR (nujol) 1607, 1558, 1456, 1248, 779, 750 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.67 (s, 2H), 7.16 (ddd, *J* = 8.0, 8.0, 1.5 Hz, 1H), 7.22–7.28 (m, 2H), 7.41–7.57 (m, 6H), 7.69 (d, *J* = 7.5 Hz, 1H), 7.80 (d, *J* = 7.5 Hz, 1H), 7.90–7.95 (m, 2 H), 8.12 (d, *J* = 8.0 Hz, 1H), 8.32 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 54.7, 116.8, 118.6, 119.0, 122.8, 123.7, 124.1, 124.8, 125.2, 125.8, 125.9, 126.1, 126.3, 127.6, 128.9, 129.0, 131.2, 131.7, 131.9, 134.1, 136.7, 151.7, 153.0, 155.2. Found: C, 85.70; H, 5.30; N, 4.21%. Calcd for $C_{24}H_{17}NO$: C, 85.94; H, 5.11; N, 4.18%. m.p.: 177–182 ˚C (decomp.).

***N*-(3-Trifluoromethylphenylmethyl)xanthone Imine (1d)**: IR (nujol) 1616, 1456, 1329, 1130, 775, 752 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.27 (s, 2H), 7.23–7.28 (m, 3H), 7.41 (dd, *J* = 8.5, 1.0 Hz, 1H), 7.46–7.55 (m, 4H), 7.73 (d, *J* = 7.0 Hz, 1H), 7.81 (s, 1H), 7.97 (dd, *J* = 8.5, 1.0 Hz, 1 H), 8.30 (dd, *J* = 8.0, 1.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 56.4, 116.8, 118.7, 122.6, 123.7 (q, $J_{C–F}$ = 3.9 Hz), 124.1, 124.5 (q, $J_{C–F}$ = 3.9 Hz), 124.5 (q, $J_{C–F}$ = 270.6 Hz), 125.5, 126.1, 128.9, 129.0, 130.8 (q, $J_{C–F}$ = 31.9 Hz), 131.0, 131.3, 132.0, 138.1, 143.0, 151.2, 152.9, 155.2. Found: C, 71.57; H, 4.17; N, 4.03%. Calcd for $C_{21}H_{14}F_3NO$: C, 71.38; H, 3.99; N, 3.96%. m.p.: 76–79 ˚C.

***N*-(2-Bromophenylmethyl)xanthone Imine (1f)**: IR (nujol) 1745, 1613, 1455, 1334, 748 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.25 (s, 2H), 7.16 (ddd, *J* = 7.5, 7.5, 1.5 Hz, 1H), 7.24–7.29 (m, 3H), 7.36 (ddd, *J* = 7.5, 7.5, 1.5 Hz, 1H), 7.41 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.49 (ddd, *J* = 7.5, 7.5, 1.5 Hz, 1H), 7.54 (ddd, *J* = 7.5, 7.5, 1.5 Hz, 1H), 7.60 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.79 (dd, *J* = 7.5, 1.5 Hz, 1H),

7.97 (dd, J = 7.5, 1.5 Hz, 1H), 8.35 (d, J = 7.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 56.9, 116.8, 118.6, 119.1, 122.8, 123.4, 124.1, 125.0, 126.2, 127.7, 128.3, 128.9, 129.3, 131.3, 132.0, 132.5, 134.7, 140.7, 152.9, 155.1. m.p.: 81–82 ˚C.

***N*-Benzhydrylxanthone Imine (2a)**: IR (nujol) 1611, 1559, 1456, 1334, 753 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.40 (s, 1H), 7.14 (dd, J = 7.5, 1.5 Hz, 1H), 7.23–7.32 (m, 4H), 7.35 (dd, J = 7.5, 7.5 Hz, 4H), 7.40–7.41 (m, 1H), 7.46–7.52 (m, 2H), 7.57 (d, J = 7.5 Hz, 4H), 7.74 (dd, J = 8.0, 1.5 Hz, 1H), 8.48 (dd, J = 8.0, 1.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 68.9, 109.9, 116.6, 118.5, 122.7, 124.0, 125.6, 126.3, 127.0, 127.5, 128.8, 128.8, 131.1, 131.7, 145.9, 150.2, 153.1, 155.3. Found: C, 86.42; H, 5.48; N, 3.89%. Calcd for $C_{26}H_{19}NO$: C, 86.40; H, 5.30; N, 3.88%. m.p.: 150–152 ˚C

***N*-(9-Xanthenyl)benzophenone Imine (2a')**: IR (nujol) 1648, 1576, 1454, 1259, 754 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.72 (s, 1H), 7.08 (dd, J = 7.0, 7.0 Hz, 2H), 7.13–7.17 (m, 4H), 7.25–7.28 (m, 2H), 7.33–7.36 (m, 2H), 7.39–7.41 (m, 3H), 7.45–7.51 (m, 3 H), 7.73–7.74 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 56.8, 116.8, 123.3 (two signals merged), 128.0 (two signals merged), 128.3, 128.6, 129.0, 129.0, 129.3, 130.7, 136.5, 139.6, 151.5, 169.4. Found: C, 86.43; H, 5.60; N, 3.64%. Calcd for $C_{26}H_{19}NO$: C, 86.40; H, 5.30; N, 3.88%. m.p. 233–236 ˚C.

Some amine hydrochlorides **3•HCl** were acylated with acid chloride in the presence of triethylamine in dichloromethane in more than 90% yield to afford analytically pure material.

Benzhydrylamine Hydrochloride (3a•HCl): IR (nujol) 1684, 1653, 1558, 1521, 1457, 739, 701 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 5.63 (s, 1H), 7.34–7.37 (m, 2H), 7.41–7.44 (m, 4H), 7.53–7.54 (m, 4H), 9.14 (s, 3H); ^{13}C NMR (DMSO-d_6) δ 57.0, 127.3, 128.3, 128.8, 138.3. Found: C, 70.79; H, 6.51; N, 6.43%. Calcd for $C_{13}H_{14}ClN$: C, 71.07; H, 6.42; N, 6.38%. m.p.: 297–304 ˚C.

***N*-(4-Methylphenyl)phenylmethylamine Hydrochloride (3b•HCl)**: IR (nujol) 1684, 1653, 1558, 1517, 1507, 1456, 699 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 2.27 (s, 3H), 5.54 (s, 1H), 7.18 (d, J = 7.0 Hz, 2H), 7.31–7.44 (m, 5H), 7.51–7.55 (m, 2H), 9.27 (s, 3H); ^{13}C NMR (DMSO-d_6) δ 56.9, 127.3, 128.1, 128.5, 128.7, 129.0, 129.2, 135.5, 125.7, 138.6. m.p.: 218–222 ˚C.

***N*-[(4-Methylphenyl)phenylmethyl]acetamide (3b•Ac)**: IR (nujol) 3303, 2853, 1653, 1539, 1456, 736 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.06 (s, 3H), 2.33 (s, 3H), 6.02 (d, J = 7.5 Hz, 1H), 6.21 (d, J = 7.5 Hz, 1H), 7.10–7.15 (m, 4H), 7.22–7.27 (m, 3H), 7.31–7.34 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 21.2, 23.6, 56.9, 127.5, 127.5, 127.6, 128.8, 129.5, 137.4, 138.8, 141.8, 169.2. Found: C, 80.41; H, 7.23; N, 5.85%. Calcd for $C_{16}H_{17}NO$: C, 80.30; H, 7.16; N, 5.85%. m.p.: 129–131 ˚C.

***N*-[(4-Methoxyphenyl)phenylmethyl]benzamide (3c•Bz)**: IR (nujol) 2855, 1558, 1507, 1457, 1247, 701 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.79 (s, 3H), 6.40 (d, *J* = 7.5 Hz, 1H), 6.64 (d, *J* = 7.5 Hz, 1H), 6.87–6.89 (m, 2H), 7.20–7.23 (m, 2H), 7.25–7.36 (m, 5H), 7.42–7.45 (m, 2H), 7.49–7.52 (m, 1H), 7.81–7.52 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 55.5, 57.1, 114.3, 127.2, 127.5, 127.6, 128.8, 128.9, 128.9, 131.8, 133.8, 134.4, 141.8, 159.2, 166.6. Found: C, 79.61; H, 5.97; N, 4.52%. Calcd for $C_{21}H_{19}NO_2$: C, 79.47; H, 6.03; N, 4.41%. m.p.: 185–187 °C.

***N*-[4-(*N*,*N*-Dimethylamino)phenyl]phenylmethylamine Dihydrochloride (3d•2HCl)**: IR (nujol) 1684, 1653, 1558, 1508, 1457 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 3.03 (s, 6H), 5.64 (s, 1H), 7.34 (dd, *J* = 7.5, 7.5 Hz, 1H), 7.41 (dd, *J* = 7.5, 7.5 Hz, 2H), 7.59–7.60 (m, 2H), 7.35–7.68 (m, 5H), 9.37 (s, 3H); ^{13}C NMR (DMSO-d_6) δ 43.9 (bs), 56.6, 124.8 (× 2C), 125.3 (× 3C), 127.4 (× 2C), 134.9. Found: C, 59.97; H, 6.56; N, 9.29%. Calcd for $C_{15}H_{20}Cl_2N_2$: C, 60.21; H, 6.74; N, 9.39%. m.p.: 214–216 °C (decomp.).

***N*-(2-Methylphenyl)phenylmethylamine Hydrochloride (3e•HCl)**: IR (nujol) 2855, 1684, 1653, 1558, 1508, 1457 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 2.26 (s, 3H), 5.69 (s, 1H), 7.22-7.47 (m, 8H), 7.69–7.70(m, 1H), 9.19 (s, 3H); ^{13}C NMR (DMSO-d_6) δ 19.2, 53.9, 126.2, 126.4, 128.2, 128.5, 128.7, 128.9, 130.8, 135.5, 136.2, 137.3. m.p.: 277–281 °C.

***N*-(2-Methylphenyl)phenylmethylacetamide (3e•Ac)**: IR (nujol) 2855, 1539, 1507, 1457, 1451 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.06 (s, 3H), 2.29 (s, 3H), 5.97 (d, *J* = 7.5 Hz, 1H), 6.40 (d, *J* = 7.5 Hz, 1H), 7.09–7.11 (m, 1H), 7.16–7.21 (m, 5H), 7.24–7.27 (m, 1H), 7.29–7.32 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 19.7, 23.5, 54.2, 126.3, 126.8, 127.6, 127.6, 127.7, 128.8, 131.0, 136.5, 139.7, 141.2, 169.0. Found: C, 80.36; H, 7.14; N, 5.87%. Calcd for $C_{16}H_{17}NO$: C, 80.30; H, 7.16; N, 5.85%. m.p.: 147–155 °C.

***N*-[Phenyl(4-vinylphenyl)methyl]benzamide (3f•Bz)**: IR (nujol) 2842, 1636, 1558, 1539, 1457, 1374 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.24 (dd, *J* = 18.0, 1.0 Hz, 1H), 5.73 (dd, *J* = 18.0, 1.0 Hz, 1H), 6.44 (d, *J* = 8.0 Hz, 1H), 6.65–6.73 (m, 2H), 7.26–7.31 (m, 5H), 7.34–7.37 (m, 2H), 7.38–7.40 (m, 2H), 7.42–7.45 (m, 2H), 7.51 (ddd, *J* = 7.0, 7.0, 1.5 Hz, 1H), 7.82 (d, *J* = 7.0 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 57.4, 114.4, 126.8, 127.2, 127.7, 127.8, 127.9, 128.8, 129.0, 131.9, 134.4, 136.5, 137.2, 141.2, 141.5, 166.6. Found: C, 84.09; H, 6.22; N, 4.39%. Calcd for $C_{22}H_{19}NO$: C, 84.31; H, 6.11; N, 4.47%. m.p.: 182–184 °C.

***N*-[Phenyl{4-(*N*,*N*-dimethylcarbamoyl)phenyl}methyl]benzamide (3g•Bz)**: IR (nujol) 2930, 1733, 1267, 1090, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.94 (s, 3H), 3.05 (s, 3H), 6.48 (d, *J* = 7.5 Hz, 1H), 7.25–7.40 (m, 12H), 7.47 (dd, *J* = 7.5, 7.5 Hz, 1H), 7.84 (d, *J* = 7.5 Hz, 2H); ^{13}C NMR

($CDCl_3$) δ 35.5, 39.7, 57.2, 127.2, 127.3, 127.4, 127.7, 128.5, 128.6, 128.7, 131.6, 134.0, 135.2, 141.0, 143.0, 166.6, 171.1.

Phenyl(2-pyridyl)methylamine Dihydrochloride (3h•2HCl): IR (nujol) 2597, 1684, 1653, 1558, 1507 cm^{-1}; ^1H NMR (DMSO-d_6) δ 5.82 (s, 1H), 7.21–7.78 (m, 7H), 8.00 (bs, 1H), 8.68 (bs, 1H), 9.39 (bs, 3H), 12.07 (bs, 1H); ^{13}C NMR (DMSO-d_6) δ 56.9, 123.2, 124.2, 127.9, 128.8, 128.9, 137.0, 139.5, 147.6, 155.6. m.p.: 230–234 °C (decomp.).

***N*-[(1-Naphthyl)phenylmethyl]benzamide (3i•Bz)**: IR (nujol) 2923, 2854, 1734, 1684, 1628, 1558, 1507, 776 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.73 (d, J = 8.0 Hz, 1H), 7.20 (d, J = 8.0 Hz, 1H), 7.29–7.36 (m, 6H), 7.40–7.44 (m, 3H), 7.48–7.51 (m, 3H), 7.80–7.84 (m, 3H), 7.88–7.90 (m, 1H), 8.07–8.09 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 54.5, 123.9, 125.4, 125.8, 126.1, 126.9, 127.3, 127.7, 127.8, 128.8, 128.9, 128.9, 129.0, 131.5, 131.9, 134.3, 134.3, 137.2, 141.3, 166.5. Found: C, 85.57; H, 5.87; N, 4.21%. Calcd for $C_{24}H_{19}NO$: C, 85.43; H, 5.68; N, 4.15%. m.p. 166–169 °C.

***N*-[Phenyl(3-trifluoromethylphenyl)methyl]benzamide (3j•Bz)**: IR (nujol) 3309, 2935, 1708, 1645, 1133, 667 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.49 (d, J = 7.5 Hz, 1H), 6.66 (d, J = 7.5 Hz, 1H), 7.27 (d, J = 7.0 Hz, 2H), 7.32–7.40 (m, 3H), 7.44-7.57 (m, 7H), 7.83 (d, J = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 57.5, 124.1 ($J_{H\text{-}F}$= 3.8 Hz), 124.6 ($J_{H\text{-}F}$= 3.8 Hz), 126.3 ($J_{H\text{-}F}$= 263 Hz), 127.2, 127.8, 128.3, 128.9, 129.3, 129.3 ($J_{H\text{-}F}$= 31 Hz), 129.4, 131.0, 132.1, 134.0, 140.8, 142.6, 166.8. Found: C, 70.95; H, 4.58%. Calcd for $C_{21}H_{16}F_3NO$: C, 70.89; H, 4.54%.

***N*-(9-Fluorenyl)acetamide (9)**: IR (nujol) 3276, 1647, 1639, 1544, 761, 746, 728 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.12 (s, 3H), 5.68 (d, J = 8.5 Hz, 1H), 6.24 (d, J = 8.5 Hz, 1H), 7.32 (ddd, J = 7.5, 7.5, 1.0 Hz, 2H), 7.41 (dd, J = 7.5, 7.5 Hz, 2H), 7.58 (dd, J = 7.5, 1.0 Hz, 2H), 7.69 (d, J = 7.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 23.7, 55.0, 120.2, 125.3, 128.0, 128.9, 140.8, 144.5, 170.9.

Figure S1. ^{1}H NMR spectrum of **1b**

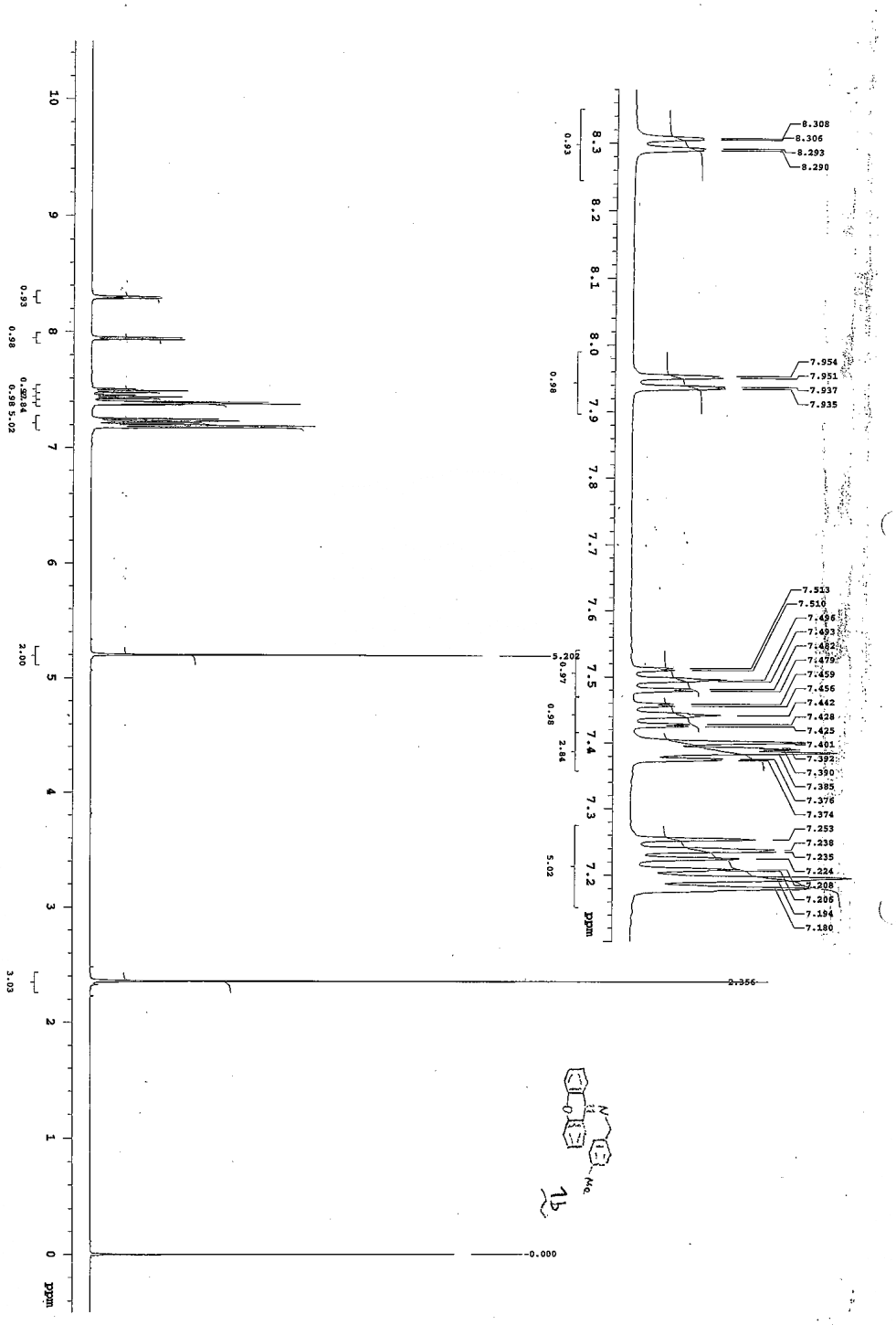

Figure S2. ^{13}C NMR spectrum of **1b**

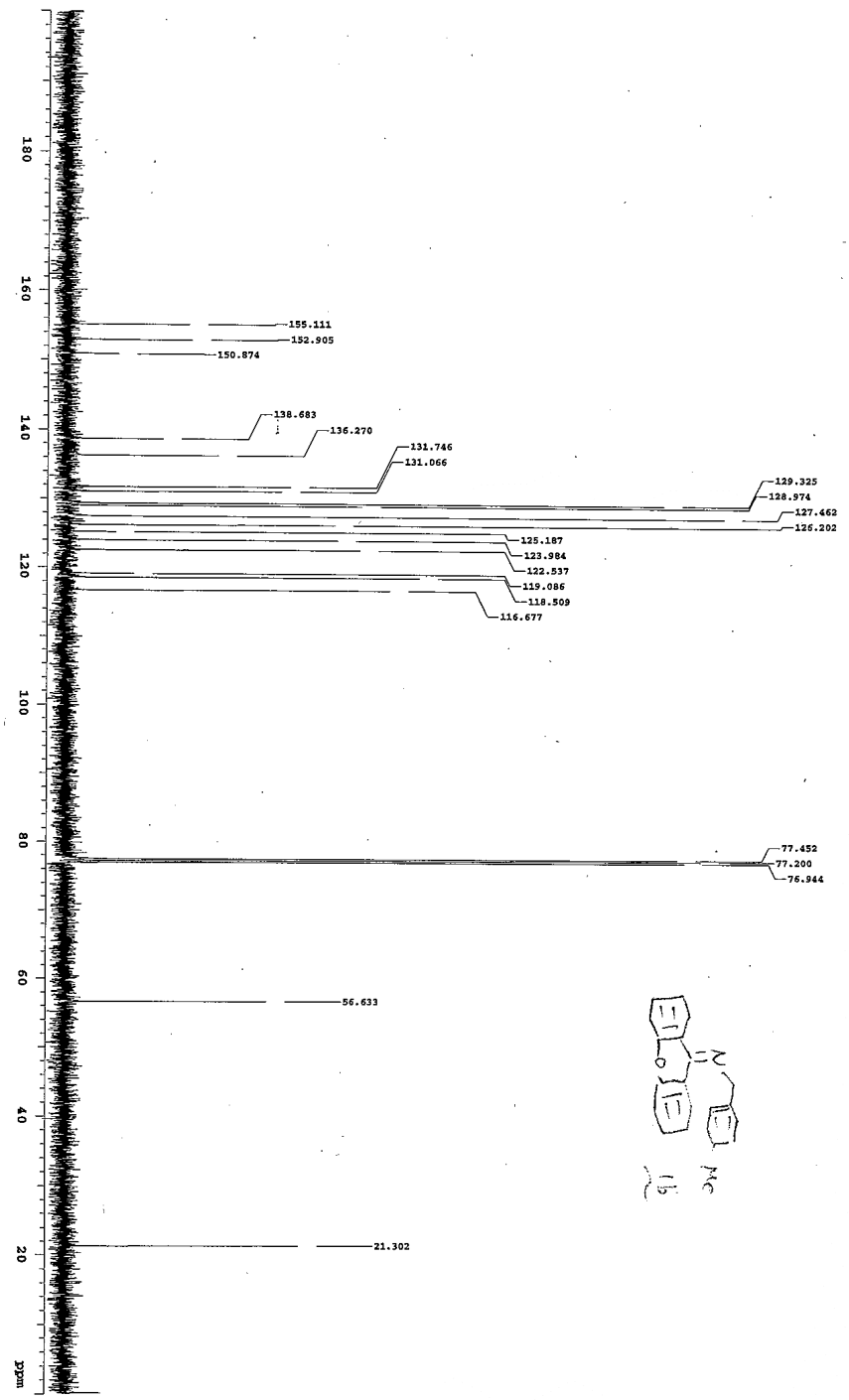

Figure S3. ^{1}H NMR spectrum of **1f**

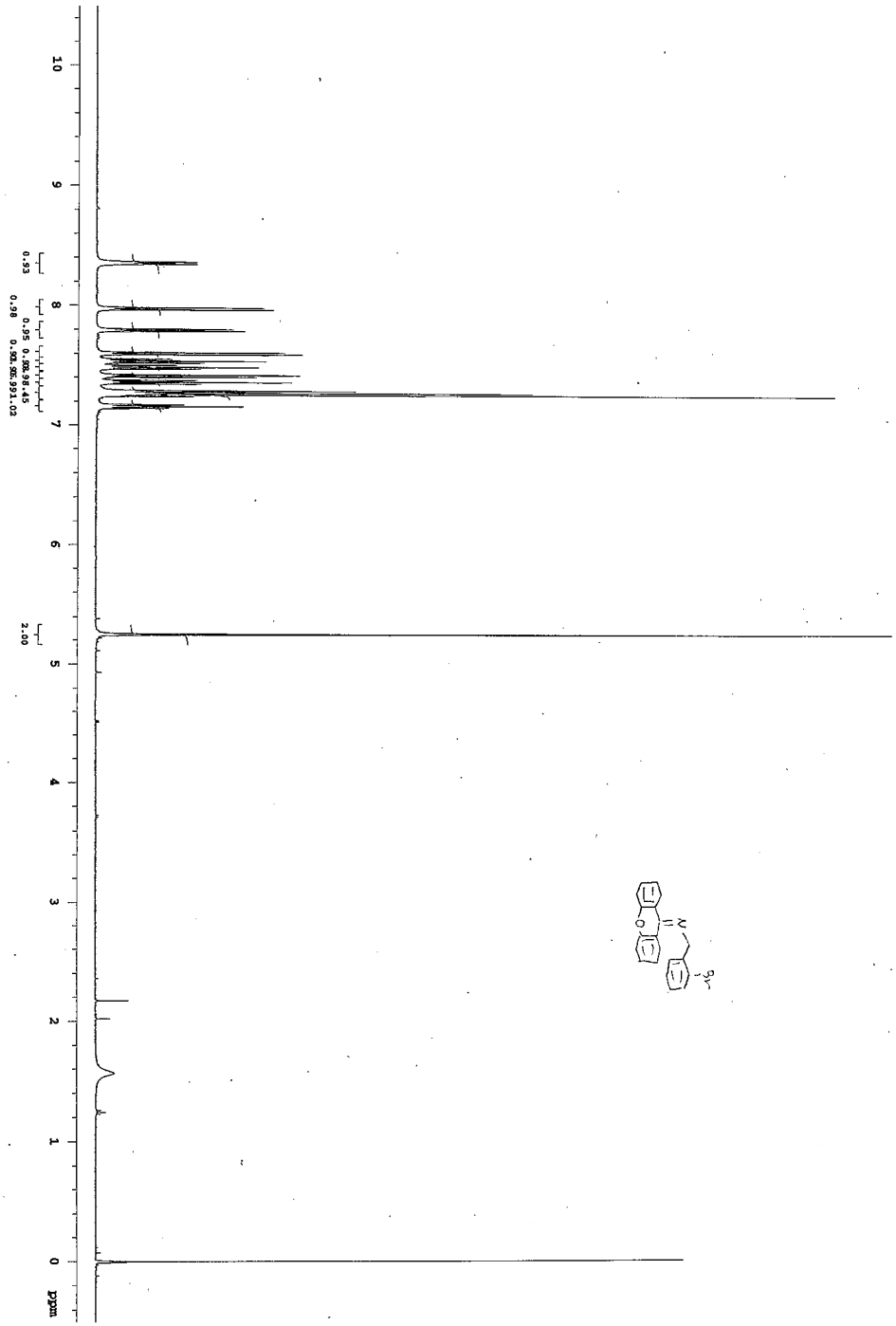

Figure S4. ^{13}C NMR spectrum of **1f**

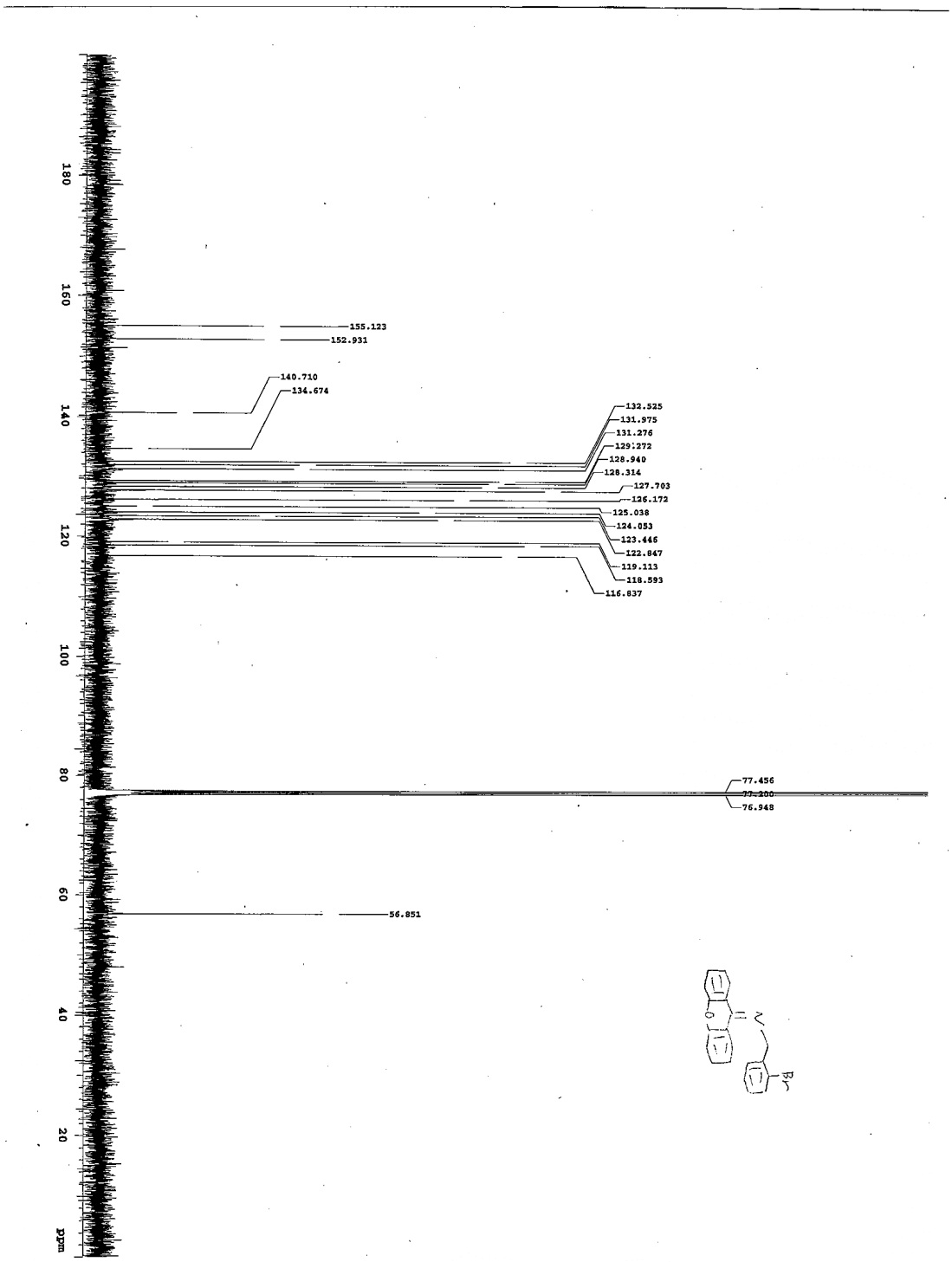

Figure S5. ^{1}H NMR spectrum of **3b•HCl**

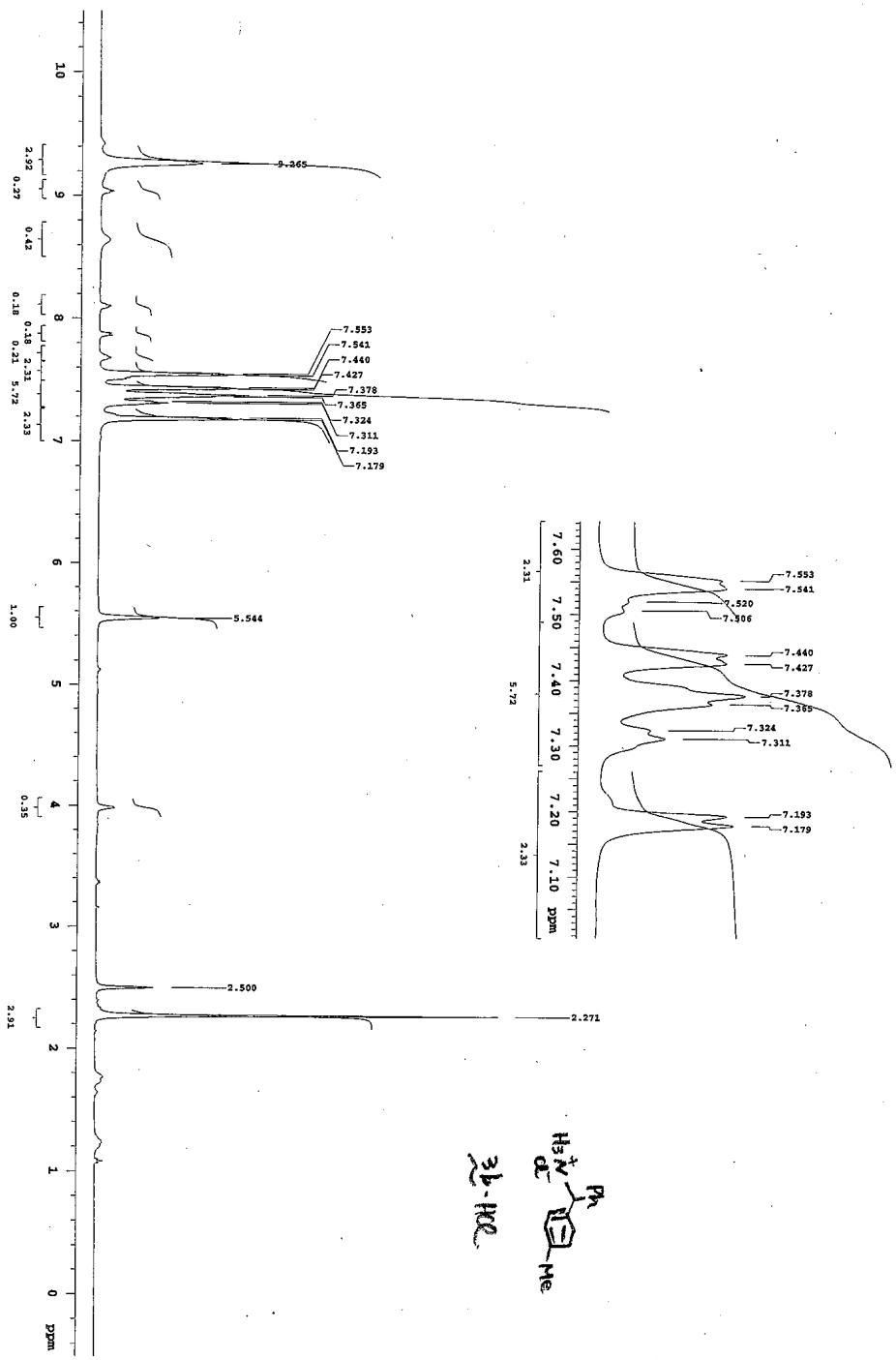

Figure S6. ^{13}C NMR spectrum of **3b•HCl**

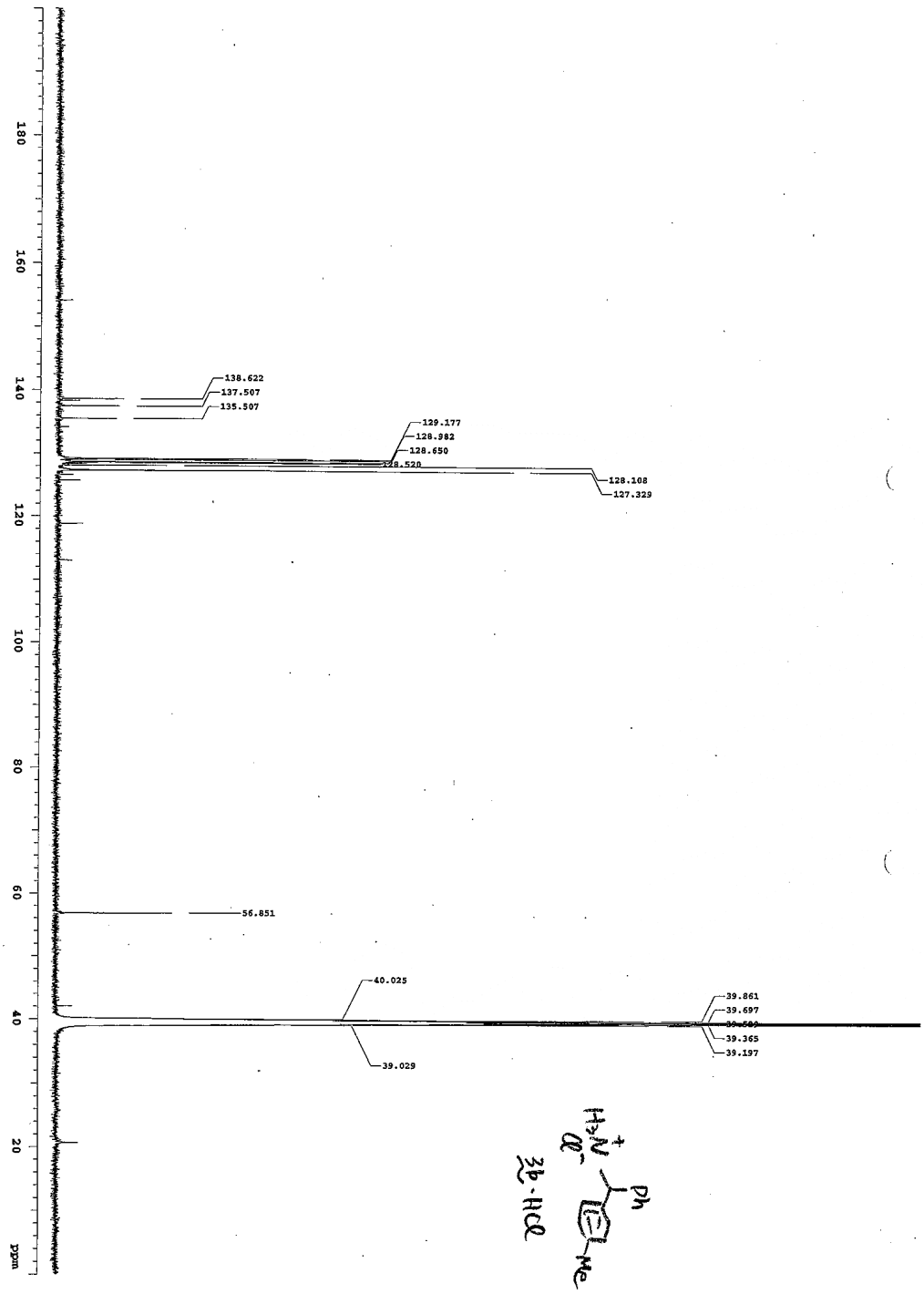

Figure S7. ^{1}H NMR spectrum of **3e•HCl**

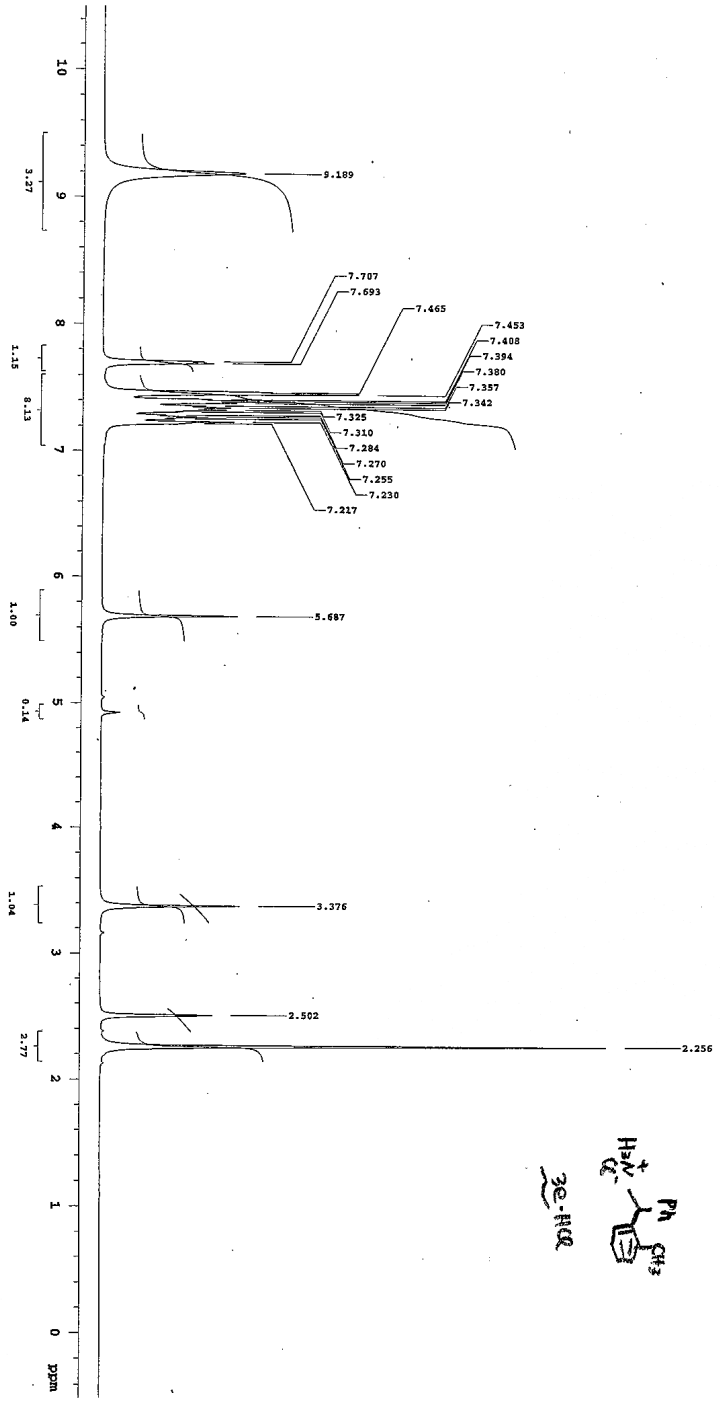

Figure S8. ^{13}C NMR spectrum of **3e•HCl**

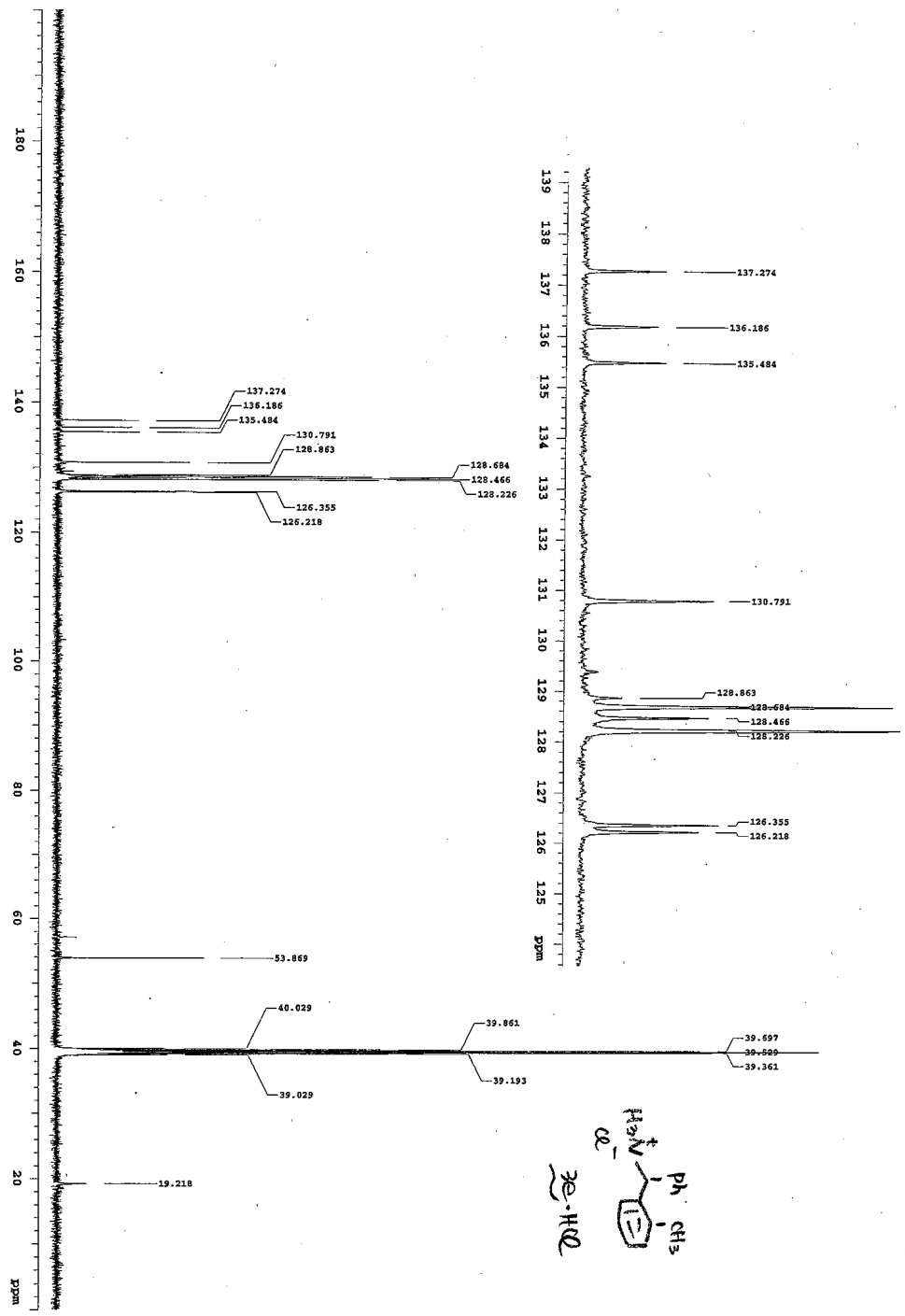

Figure S9. ^{1}H NMR spectrum of **3g•Bz**

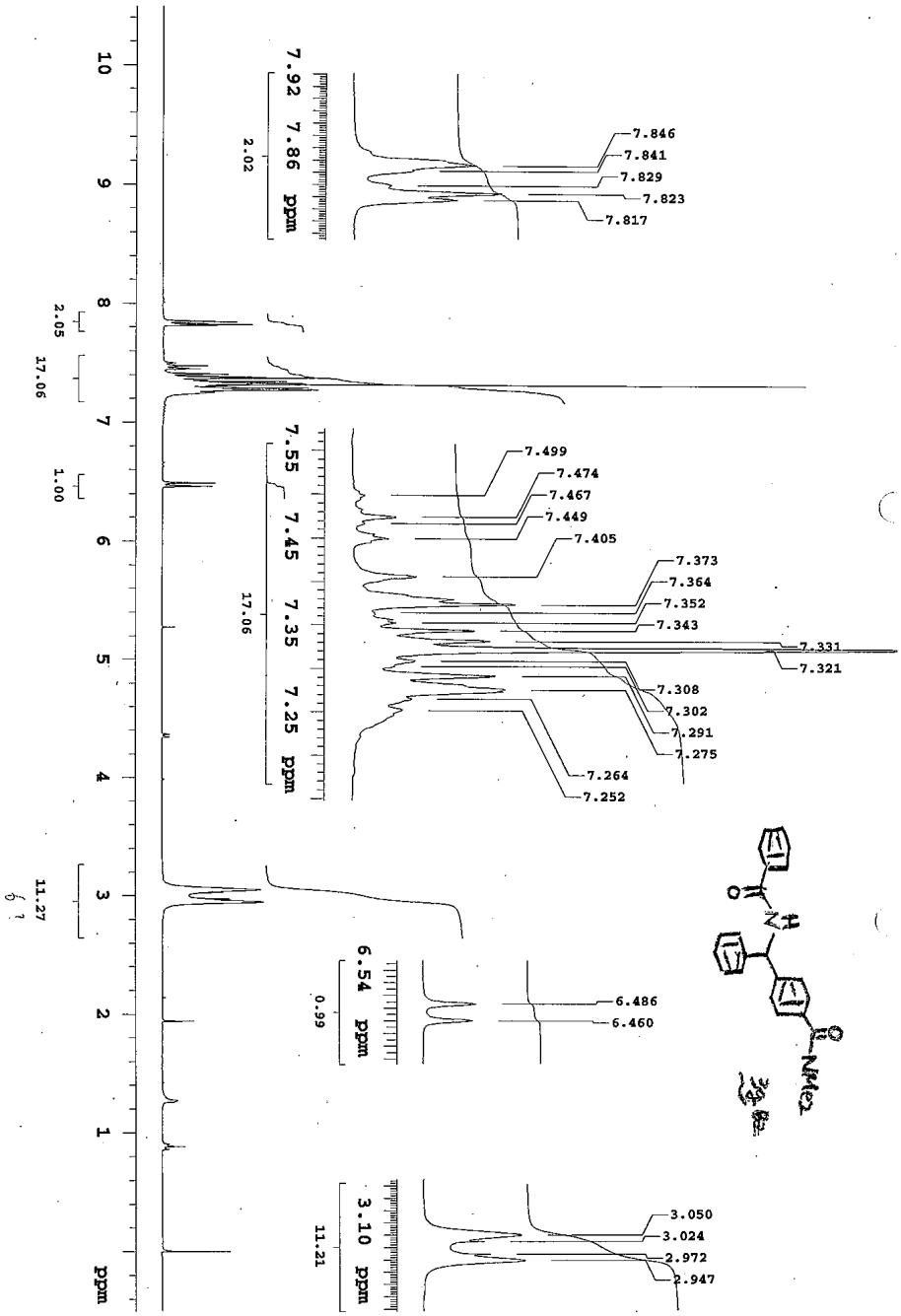

Figure S10. ^{13}C NMR spectrum of **3g•Bz**

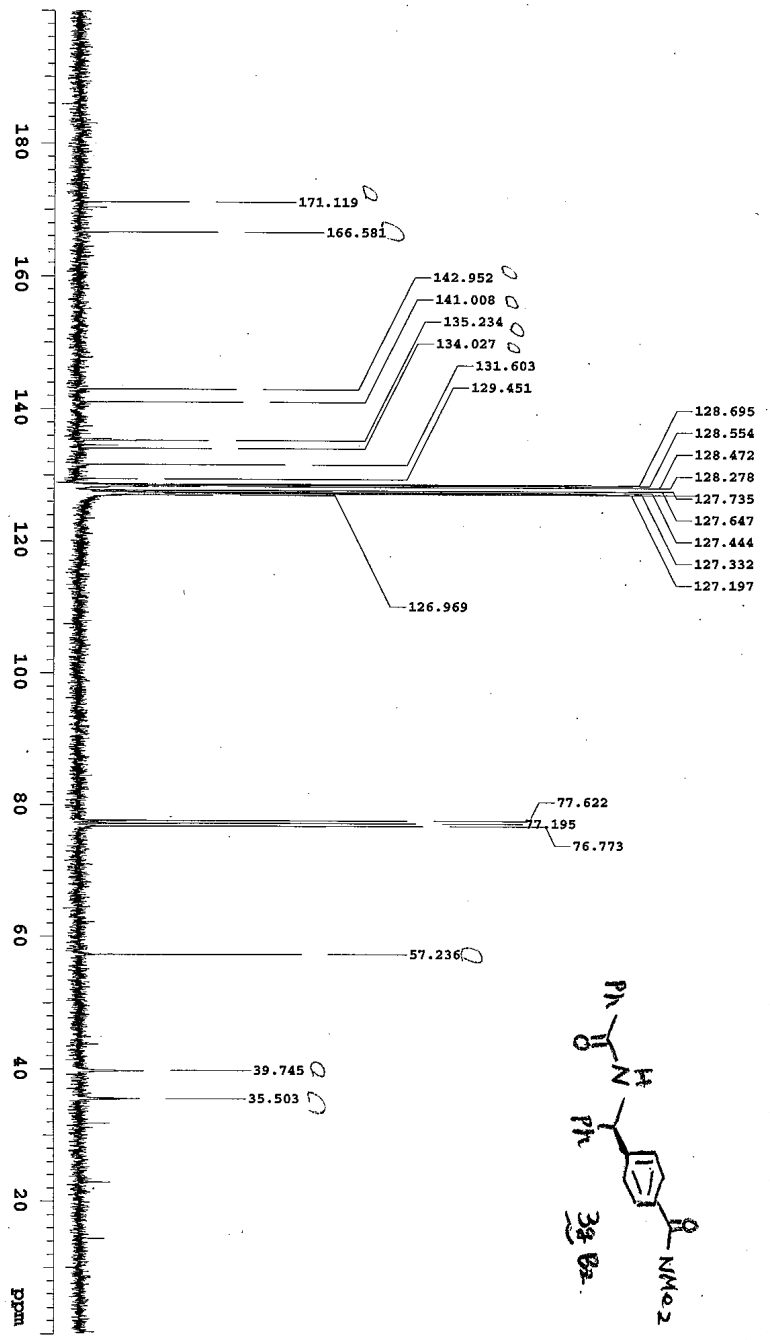

Figure S11. ^{1}H NMR spectrum of **3h•2HCl**

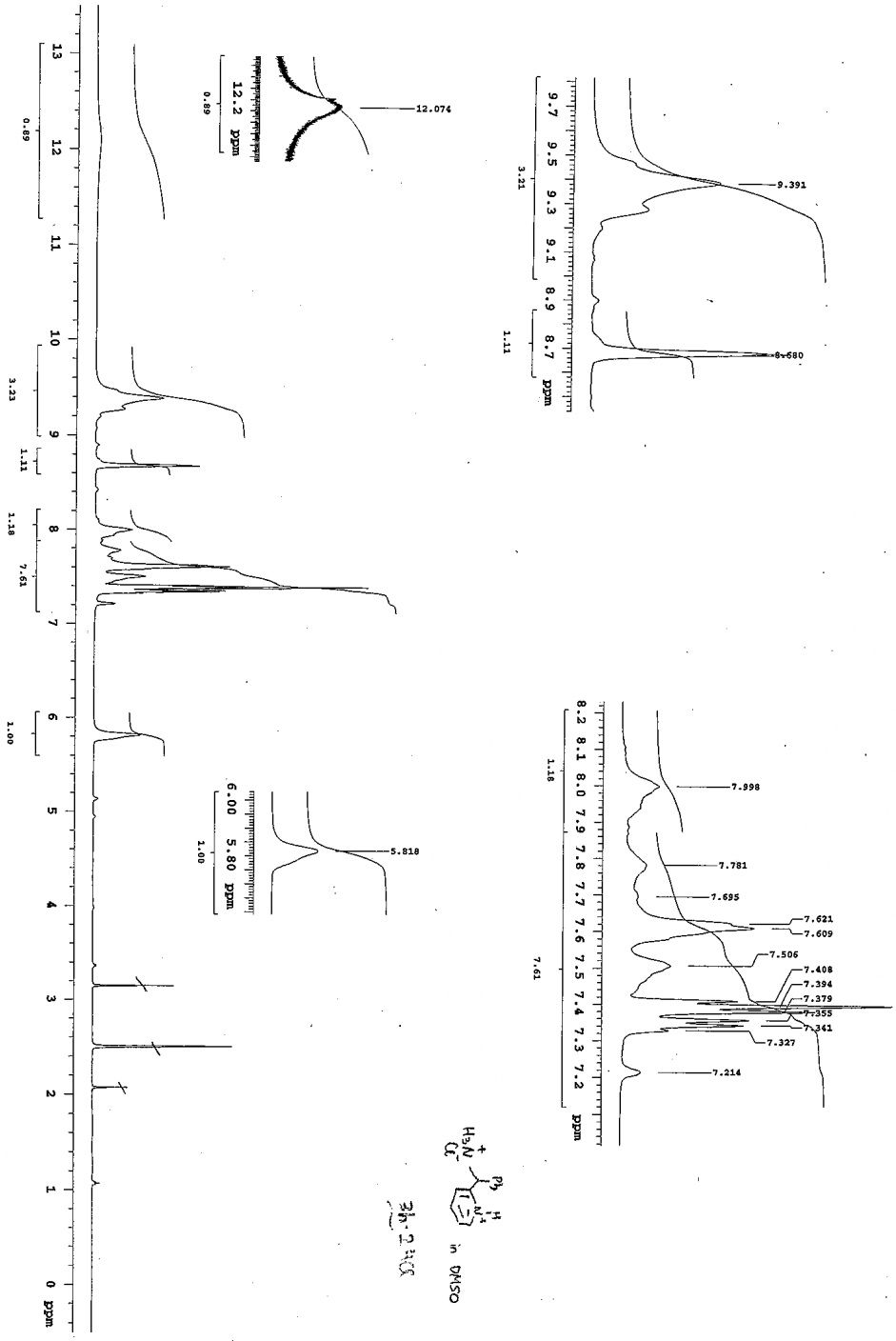

Figure S12. ^{13}C NMR spectrum of **3h•2HCl**

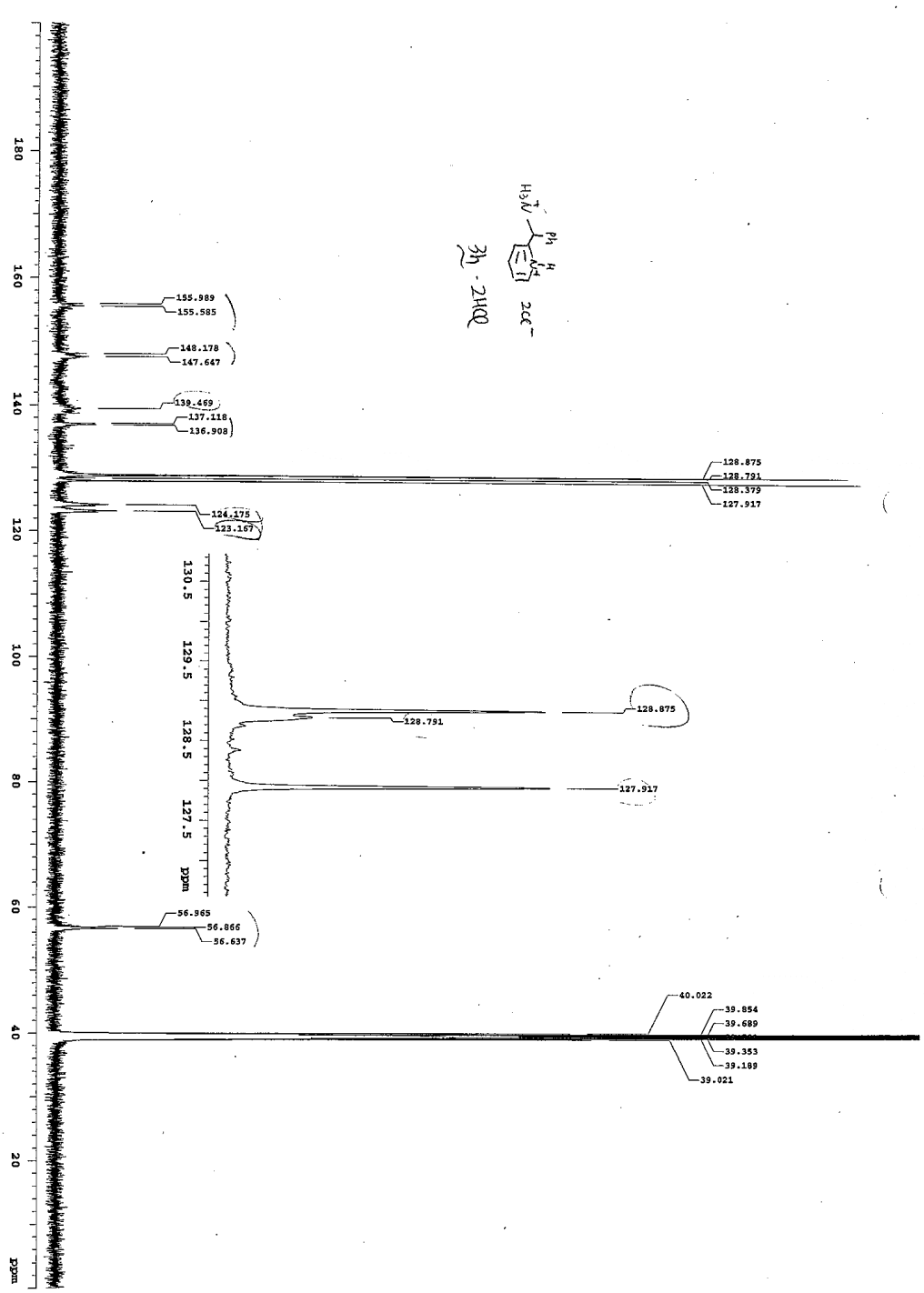

Figure S13. ^{1}H NMR spectrum of **9**

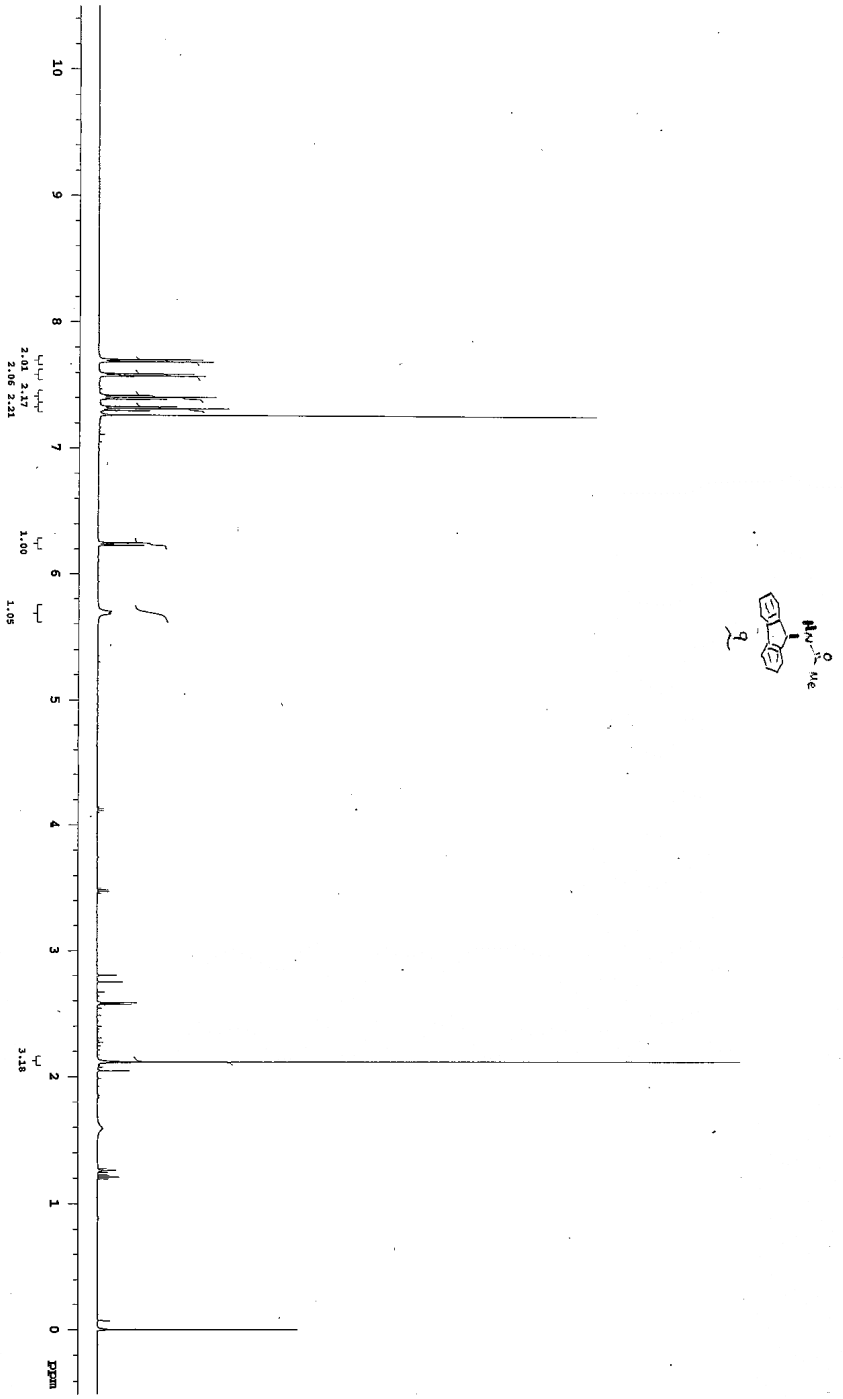

Figure S14. ^{13}C NMR spectrum of **9**