Supporting Information

Bis-tridentate Ru(II) Sensitizers with Spatially Encumbered 2,6-Dipyrazolylpyridine Ancillary for Dye-Sensitized Solar Cells

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Experimental Section

General procedures: All reactions were performed under argon atmosphere and solvents were distilled from appropriate drying agents prior to use. Commercially available reagents were used without further purification unless otherwise stated. All reactions were monitored using pre-coated TLC plates (0.20 mm with fluorescent indicator UV254). Mass spectra were obtained on a JEOL SX-102A instrument operating in electron impact (EI) or fast atom bombardment (FAB) mode. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury-400 or an INOVA-500 instrument. Elemental analysis was carried out with a Heraeus CHN-O Rapid Elementary Analyzer.

Synthesis of pentyl perfluorobutyrate:

Perfluorobutyric acid (25 g, 117 mmol) was mixed with 1-pentanol (20.6 g, 234 mmol), followed by dropwise addition of sulfuric acid (5.7 g, 58.4 mmol) at 0 °C. The mixture was stirred at 100 °C for 24 hours. After then, the content was poured over an ice-water mixture. The mixture was stirred 30 minutes at RT, extracted with CH_2Cl_2 (100 mL x 2), washed with a saturated solution of $NaHCO_3$ (30 mL x 2), water (200 mL x 2) and brine (200 mL x 2). The combined organic layers were dried over Na_2SO_4, and distilled under vacuum (33 ~ 37 °C, 6.59 mmHg) to yield pentyl perfluorobutyrate (26.5 g, 80 %) as a colorless liquid. ^{1}H NMR (400MHz, $CDCl_3$, 298K): δ 4.35 (t, *J* = 6.8 Hz, 2H), 1.74 ~ 1.70 (m, 2H), 1.36 ~ 1.33 (m, 4H), 0.89 (t, *J* = 6.8 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$, 298K): δ −81.08 (t, *J* = 8.6 Hz, 3F), −119.56 ~ −119.65 (m, 2F),

−127.22 ~ −127.30 (m, 2F).

Pentyl perfluorohexanoate:

It was synthesized in an analogous manner and purified by vacuum distillation (53 ~ 55 °C, 5.48 mmHg); yield: 73 %. ^{1}H NMR (400MHz, $CDCl_3$, 298K): δ 4.35 (t, *J* = 7 Hz, 2H), 1.76 ~ 1.69 (m, 2H), 1.36 ~ 1.32 (m, 4H), 0.89 (t, *J* = 7.0 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$, 298K): δ −81.04 (t, *J* = 9.6 Hz, 3F), −118.67 ~ −118.74 (m, 2F), −122.80 ~ −122.83 (m, 2F), −123.05 ~ −123.07 (m, 2F), −126.38 ~ −126.41 (m, 2F).

Pentyl perfluorooctanoate:

It was synthesized in an analogous manner and purified by vacuum distillation (73 ~ 75 °C, 4.88 torr); yield: 73 %. ^{1}H NMR (400MHz, $CDCl_3$, 298K): δ 4.35 (t, *J* = 7 Hz, 2H), 1.75 ~ 1.69 (m, 2H), 1.37 ~ 1.28 (m, 4H), 0.89 (t, *J* = 7.0 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$, 298K): δ −81.00 (t, *J* = 9.8 Hz, 3F), −118.61 ~ −118.68 (m, 2F), −121.81 (s, 2F), −122.16 (s, 2F), −122.84 (s, 4F), −126.29 (s, 2F).

Synthesis of L-tBu_C_3F_7:

A solution of *t*-BuOK (3.38 g, 30.12 mmol) in dry THF (20 mL) under N_2 was slowly added a solution of 2,6-diacetyl-4-*t*-butyl pyridine (2.2 g, 10.32 mmol) in dry THF (20 mL), and the mixture was stirred at 0 °C for 20 min. Pentyl perfluorobutyrate (8.55 g, 30.10 mmol) was next added and the mixture was heated to reflux for 24 hours. After cooling, the mixture was neutralized with 2 N HCl (aq), the content was extracted with ethyl acetate (30 mL x 2), washed with water (30 mL x 2), dried over Na_2SO_4 and evaporated to dryness The crude product was reacted with hydrazine (3 mL, 60 mmol) in refluxing EtOH (50 mL) overnight, and the solvent was removed *in vacuo*. The mixture was extracted with CH_2Cl_2 (30 mL x 2), washed with water (30 mL x 2) and dried over Na_2SO_4. The solid was purified by silica gel column chromatography, eluting with ethyl acetate/hexane, 1 : 3, to give **L-tBu_C_3F_7** as white solid (4.93 g, 80 %). MS (FAB): m/z 603.2 (M^+). ^{1}H NMR (400 MHz, $CDCl_3$, 298K): δ 12.43 (s, 2H), 7.58 (s, 2H), 6.99 (s, 2H), 1.40 (s, 9H). ^{19}F NMR (376 MHz, $CDCl_3$, 298K): δ −80.32 (t, *J* = 9.4 Hz, 6F), −111.03 ~ −111.11 (m, 4F), −127.12 (s, 4F).

L-tBu_C_5F_{11}:

The same procedure was used as in the synthesis of **L-tBu_C_3F_7**, starting from *t*-BuOK (0.54 g, 4.76 mmol), pentyl perfluorohexanoate (1.83 g, 4.76 mmol) and 2,6-diacetyl-4-*t*-butyl pyridine (0.348 g, 1.59 mmol); yield: 4.3 g, 34 %. MS (FAB): m/z 803.1 (M^+). ^{1}H NMR (400MHz, d_6-acetone, 298K): δ 13.79 (s, 2H), 8.10 (s, 2H), 7.58 (s, 2H), 1.45 (s, 9H). ^{19}F NMR (376 MHz, d_6-acetone, 298K): δ −81.73 (t, *J* = 10 Hz, 6F), −109.70 ~ −109.77 (m, 4F), −122.87 ~ −122.96 (m, 4F), −123.26 ~ −123.35 (m, 4F), −126.87 ~ −126.96 (m, 4F).

L-tBu_C_7F_{15}:

The same procedure was used as in the synthesis of **L-tBu_C_3F_7**, starting from *t*-BuOK (2.30 g, 20.5 mmol), pentyl perfluorooctanoate (9.94 g, 20.5 mmol) and 2,6-diacetyl-4-*t*-butyl pyridine (1.50 g, 6.84 mmol); yield: 2.75 g, 40 %. MS (FAB): m/z 1003.3 (M^+). ^{1}H NMR (400MHz, d_6-acetone, 298K): δ 13.79 (s, 1H), 8.11 (s, 2H), 7.59 (s, 2H), 1.46 (s, 9H). ^{19}F NMR (376 MHz, d_6-acetone, 298K): δ −81.69 (t, *J* = 10 Hz, 6F), −109.62 ~ −109.7 (m, 4F), −121.90 (s, 4F), −122.59 (s, 4F), −123.04 (s, 4F), −123.29 (s, 4F), −126.75 (s, 4F).

Synthesis of TF-2'_CF_3:

A mixture of 4-(5-dodecylthiophen-2-yl)-2,6-bis(3-trifluoromethyl-1H-pyrazol-5-yl)pyridine (234 mg, 0.45 mmol), Ru(tectpy)Cl_3 (300 mg, 0.45 mmol) and 4-ethylmorpholine (0.15 mL, 1.17 mmol) in 30 mL of ethanol was heated at 80 °C under stirring for 20 h. After removal of solvent, the residue was extracted with CH_2Cl_2 (25 mL x 3), washed with water and concentrated to dryness. The crude product was further purified by silica gel column chromatography (hexane/ethyl acetate = 1:1). After then, the resulting solid was dissolved in a mixture of acetone (50 mL) and 1 M NaOH solution (6.2 mL). The mixture was heated to 60 °C under N_2 for 3 h. The solvent was removed, and the residue was dissolved in H_2O solution (10 mL). This solution was titrated with 2 N HCl to pH = 3 to afford a black precipitate. This black product was washed with CH_2Cl_2 and acetone, giving **TF-2'_CF_3** (0.26 g, 67 %). ^{1}H NMR (400MHz, d_6-DMSO, 298K): δ 9.33 (s, 2H), 9.13 (s, 2H), 8.35 (s, 2H), 7.97 (d, *J* = 3.6 Hz, 1H), 7.71 ~ 7.68 (m, 4H), 7.35 (s, 2H), 7.10 (d, *J* = 3.6 Hz, 1H), 2.95 (t, *J* = 8 Hz, 2H), 1.73 (q, J_{HH} = 6.8 Hz, 2H), 1.41-1.31 (m, 18H), 0.88 (t, *J* = 6.8 Hz, 3H). ^{19}F NMR (376 MHz, d_6-DMSO, 298K): δ −58.52 (s, 6F). Anal. Calcd. for $C_{47}H_{42}F_6N_8O_6RuS\cdot 3H_2O$: C, 53.15; N, 10.55; H, 3.99.

Found: C, 53.39; N, 10.14; H, 3.59.

Synthesis of TF-2'_C_3F_7:

A mixture of 4-(5-dodecylthiophen-2-yl)-2,6-bis(3-heptafluoropropyl-1H-pyrazol-5-yl)pyridine (0.9 g, 1.2 mmol), Ru(tectpy)Cl_3 (740 mg, 1.2 mmol) and potassium acetate (0.55 g, 5.6 mmol) in 30 mL of ethanol was heated at 80 °C under stirring for 20 h. After the removal of solvent, the residue was extracted with CH_2Cl_2 (3 x 25 mL), washed with water and concentrated to dryness. The crude product was further purified by silica gel column chromatography (hexane/ethyl acetate = 1:1). After then, the resulting solid was dissolved in a mixture of acetone (50 mL) and 1 M NaOH solution (6.2 mL). The mixture was heated to 60 °C under N_2 for 3 h. The solvent was removed, and the residue was dissolved in H_2O solution (10 mL). This solution was titrated with 2 N HCl to pH = 3 to afford a black precipitate. This black product was washed with CH_2Cl_2 and acetone, giving **TF-2'_C_3F_7** (1.3 g, 85 %). ^{1}H NMR (400MHz, d_6-DMSO, 298K): δ 13.92 (s, 3H), 9.32 (s, 2H), 9.10 (s, 2H), 8.36 (s, 2H), 7.98 (d, *J* = 3.6 Hz, 1H), 7.68 ~ 7.64 (m, 4H), 7.33 (s, 2H), 7.10 (d, *J* = 3.6Hz, 1H), 2.95 (t, *J* = 7.2 Hz, 2H), 1.72 (q, *J* = 7.2 Hz, 2H), 1.42 ~ 1.35 (m, 18H), 0.83 (t, J_{HH} = 7.2 Hz, 3H). ^{19}F NMR (376 MHz, d_6-DMSO, 298K): −80.21 (t, *J* = 8.0 Hz, 6F), −107.26 (s, 4F), −127.05 (s, 4F). Anal. Calcd. for $C_{51}H_{42}F_{14}N_8O_6RuS{\cdot}3H_2O$: C, 48.13; N, 9.10; H, 3.78. Found: C, 48.54; N, 8.88; H, 3.35.

Synthesis of TF-tBu(Et)_C_3F_7:

A mixture of **L-tBu_C_3F_7** (0.93 g, 1.52 mmol), Ru(tectpy)Cl_3 (1.0 g, 1.52 mmol) and KOAc (0.75 g, 7.61 mmol) in 30 mL of xylenes was heated at 140 °C under stirring for 20 h. After removal of solvent, the crude product was purified by silica gel column chromatography (ethyl acetate/CH_2Cl_2 = 1:6) to give the ethoxy complex **TF-tBu(Et)_C_3F_7** (1.46 g, 83 %). MS (FAB, ^{102}Ru): m/z 1152.2 (M^+). ^{1}H NMR (400MHz, $CDCl_3$, 298K): δ 8.96 (s, 2H), 8.73 (s, 2H), 7.71 (s, 2H), 7.60 ~ 7.55 (m, 4H), 6.89 (s, 2H), 4.59 (q, *J* = 7.0 Hz, 2H), 4.40 (q, *J* = 7.0 Hz, 4H), 1.60 (s, 9H), 1.55 (t, *J* = 7.0 Hz, 3H), 1.36 (t, *J* = 7.0 Hz, 6H). ^{19}F NMR (376 MHz, $CDCl_3$, 298K): δ −80.60 (t, *J* = 9.0 Hz, 6F), −108.82 ~ −108.89 (m, 4F), −127.36 (s, 4F).

Synthesis of TF-tBu_C_3F_7:

The ethoxy complex **TF-tBu(Et)_C_3F_7** (1.0 g, 0.86 mmol) was dissolved in a mixture of

acetone (60 mL) and 1 M NaOH solution (25 mL). The mixture was stirred at RT under N_2 overnight. The solvent was removed, and the residue was dissolved in H_2O (5 mL). This solution was titrated with 2 N HCl(aq) to pH = 3 to produce a brown precipitate. This precipitate was washed with acetone and diethylether giving the final product **TF-tBu_C_3F_7** (0.85 g, 91 %). MS (FAB, ^{102}Ru): m/z 1068.1 (M^+). ^{1}H NMR (400MHz, d_6-DMSO, 298K): δ 13.92 (br, 1H), 9.37 (s, 2H), 9.13 (s, 2H), 8.16 (s, 2H), 7.70 (d, *J* = 5.8 Hz, 2H), 7.56 (d, *J* = 5.8 Hz, 2H), 7.28 (s, 2H), 1.58 (s, 9H). ^{19}F NMR (376 MHz, d_6-DMSO, 298K): δ −80.18 (t, *J* = 8.4 Hz, 6F), −107.29 (s, 4F), −127.09 (s, 4F). Anal. Calcd. for $C_{39}H_{24}F_{14}N_8O_6Ru$: C, 43.87; N, 10.49; H, 2.27. Found: C, 44.05; N, 10.50; H, 2.33.

TF-tBu(Et)_C_5F_{11}:

The same procedure was used as in the synthesis of **TF-tBu(Et)_C_3F_7**, starting from **L-tBu_C_5F_{11}** (0.180 g, 0.224 mmol), Ru(tectpy)Cl_3 (0.147 g, 0.224 mmol) and KOAc (0.11 g, 1.12 mmol); yield: 0.22 g, 73 %. MS (FAB, ^{102}Ru): m/z 1352.2 (M^+). ^{1}H NMR (400MHz, $CDCl_3$, 298K): δ 8.95 (s, 2H), 8.72 (s, 2H), 7.70 (s, 2H), 7.60 ~ 7.55 (m, 4H), 6.88 (s, 2H), 4.64 (q, *J* = 7.0 Hz, 2H), 4.41 (q, *J* = 7.0 Hz, 4H), 1.60 (s, 9H), 1.57 (t, *J* = 7.0 Hz, 3H), 1.38 (t, *J* = 7.0 Hz, 6H). ^{19}F NMR (376 MHz, $CDCl_3$, 298K): δ −81.00 (t, *J* = 6 Hz, 6F), −108.13 (s, 4F), −122.91 (s, 4F), −123.51 (s, 4F), −126.44 (s, 4F).

TF-tBu_C_5F_{11}:

The same procedure was used as in the synthesis of **TF-tBu_C_3F_7**, starting from **TF-tBu(Et)_C_5F_{11}** (99 mg, 0.073 mmol); yield: 79 mg, 85 %. ^{1}H NMR (400MHz, d_6-DMSO, 298K): δ 13.88 (br, 2H), 9.32 (s, 2H), 9.10 (s, 2H), 8.17 (s, 2H), 7.69 (d, *J* = 5.8 Hz, 2H), 7.56 (d, *J* = 5.8 Hz, 2H), 7.28 (s, 2H), 1.59 (s, 9H). ^{19}F NMR (376 MHz, d_6-DMSO, 298K): δ −80.58 (t, *J* = 9.6 Hz, 6F), −106.65 (s, 4F), −122.82 (s, 4F), −123.58 (s, 4F), −126.20 (s, 4F). Anal. Calcd. for $C_{43}H_{24}F_{22}N_8O_6Ru$: C, 40.74; N, 8.84; H, 1.91. Found: C, 40.85; N, 8.79; H, 2.25.

TF-tBu(Et)_C_7F_{15}:

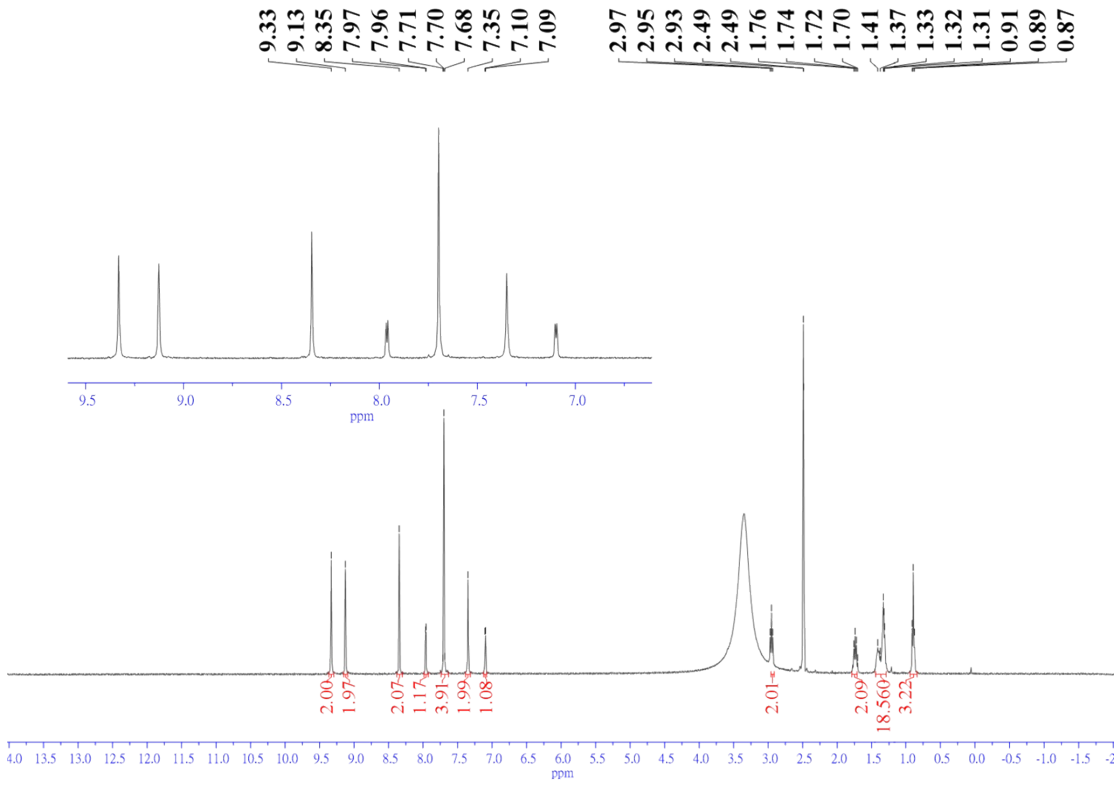
The same procedure was used as in the synthesis of **TF-tBu(Et)_C_3F_7**, starting from **L-tBu_C_7F_{15}** (0.20 g, 0.20 mmol), Ru(tectpy)Cl_3 (0.13 g, 0.20 mmol) and KOAc (0.10 g, 1.02 mmol); yield: 0.24 g, 77 %. MS (FAB, ^{102}Ru): m/z 1552.2 (M^+). ^{1}H NMR (400MHz, $CDCl_3$, 298K): δ 8.94 (s,

2H), 8.72 (s, 2H), 7.70 (s, 2H), 7.61 ~ 7.55 (m, 4H), 6.88 (s, 2H), 4.63 (q, J_{HH} = 7.2 Hz, 2H), 4.39 (q, J_{HH} = 7.2 Hz, 4H), 1.61 (s, 9H), 1.58 (t, *J* = 7.2 Hz, 3H), 1.37 (t, *J* = 7.2 Hz, 6H). ^{19}F NMR (376 MHz, $CDCl_3$, 298K): δ −80.85 (t, *J* = 9.8 Hz, 6F), −107.98 (s, 4F), −121.93 (s, 4F), −122.24 (s, 4F), −122.98 (s, 4F), −123.14 (s, 4F), −126.21 (s, 4F).

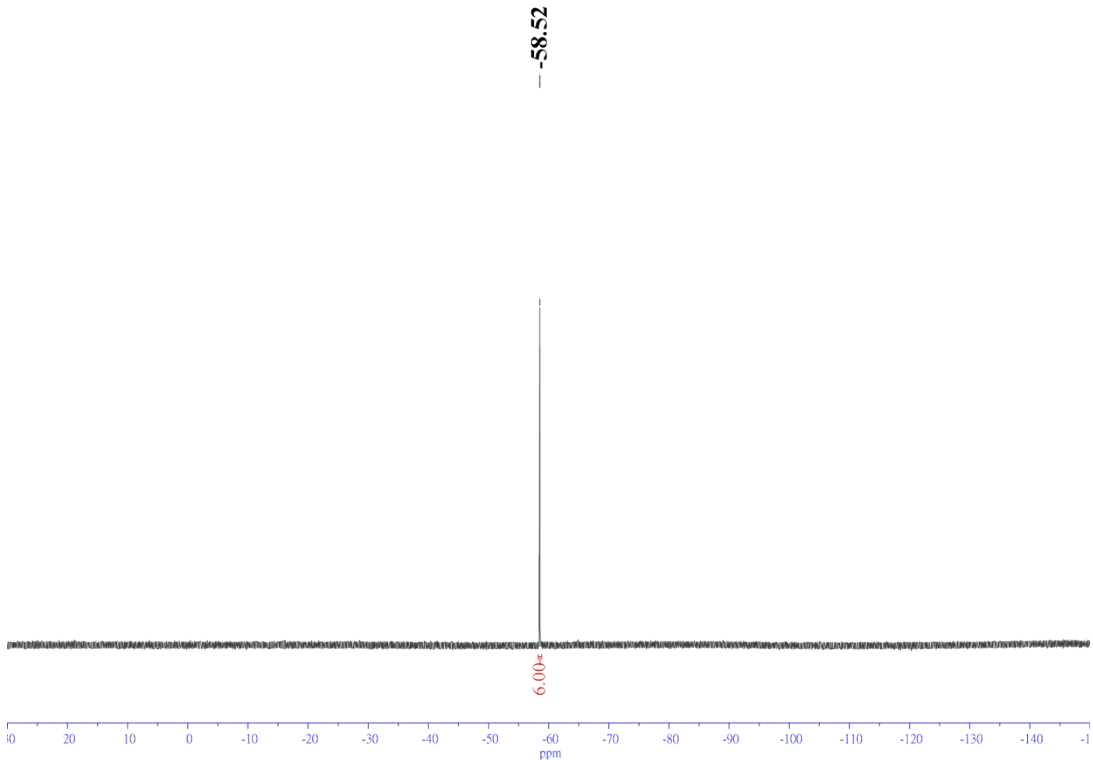
TF-tBu_C_7F_{15}:

The same procedure was used as in the synthesis of **TF-tBu_C_3F_7**, starting from **TF-tBu(Et)_C_7F_{15}** (239 mg, 0.154 mmol); yield: 190 mg, 84 %. ^{1}H NMR (400MHz, d_7-DMF, 298K): δ 9.41 (s, 2H), 9.22 (s, 2H), 8.36 (s, 2H), 7.89 (d, *J* = 5.8 Hz, 2H), 7.80 (d, J = 5.8 Hz, 2H), 7.45 (s, 2H), 1.65 (s, 9H). ^{19}F NMR (376 MHz, d_7-DMF, 298K): δ −81.32 (t, *J* = 10 Hz, 6F), −107.29 (s, 4F), −122.21 (s, 4F), −122.59 (s, 4F), −123.26 (s, 8F), −126.55 (s, 4F). Anal. Calcd. for $C_{47}H_{24}F_{30}N_8O_6Ru$: C, 38.46; N, 7.63; H, 1.65. Found: C, 38.51; N, 7.63; H, 2.01.

^{1}H NMR spectrum of TF-2'_CF_3 in d_6-DMSO



^{19}F NMR spectrum of TF-2'_CF_3 in d_6-DMSO



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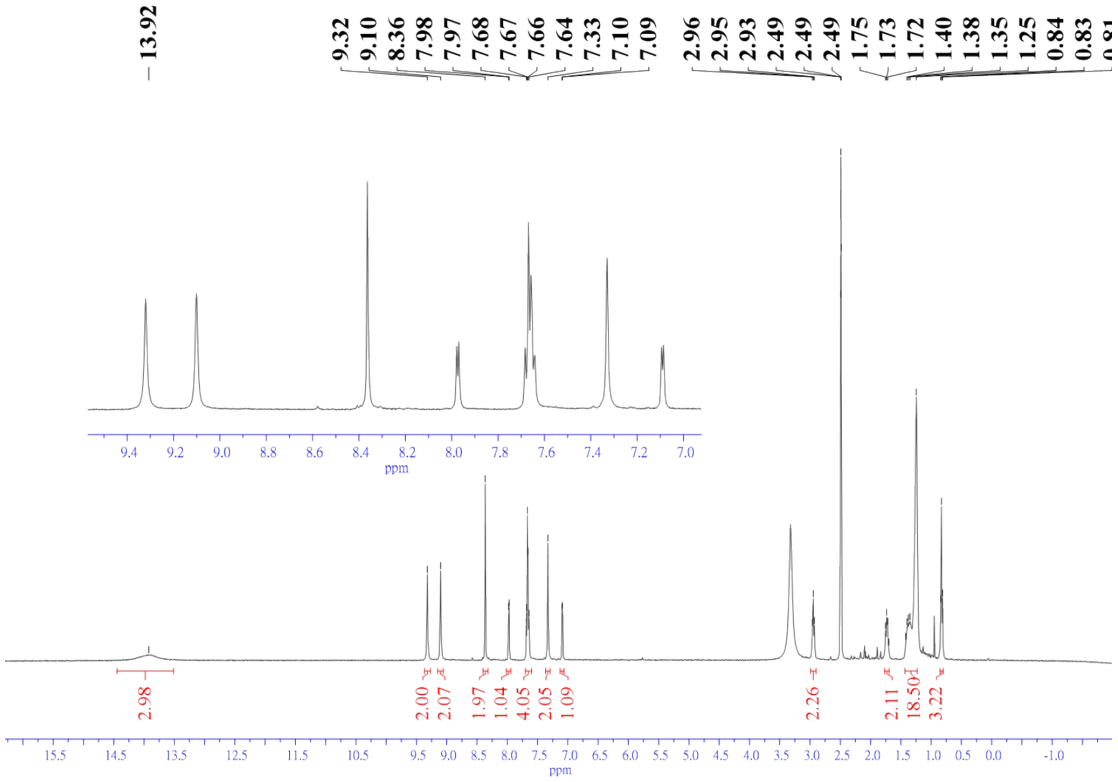

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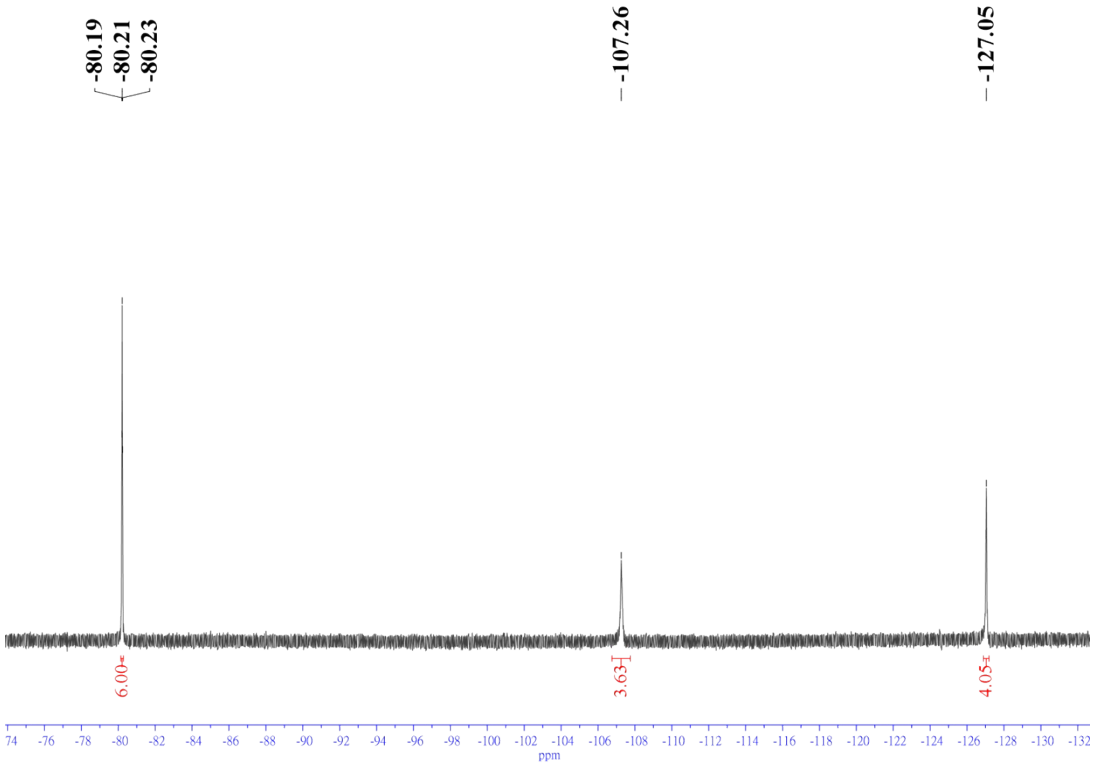

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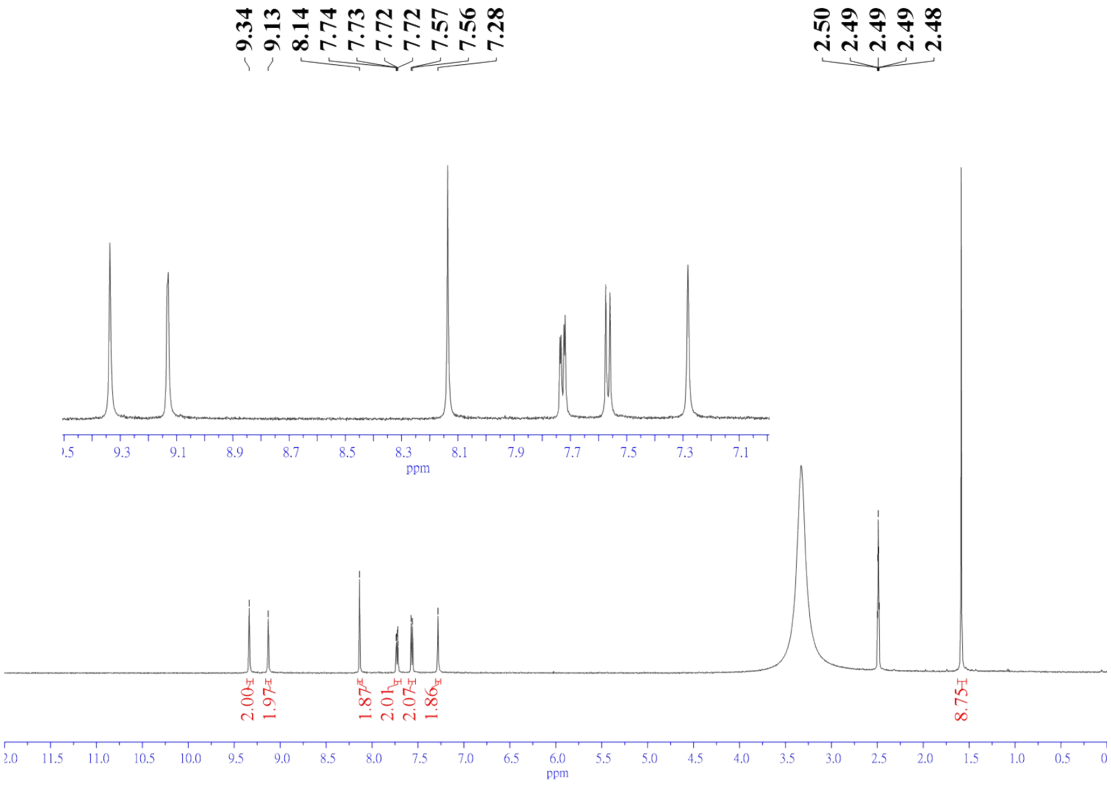

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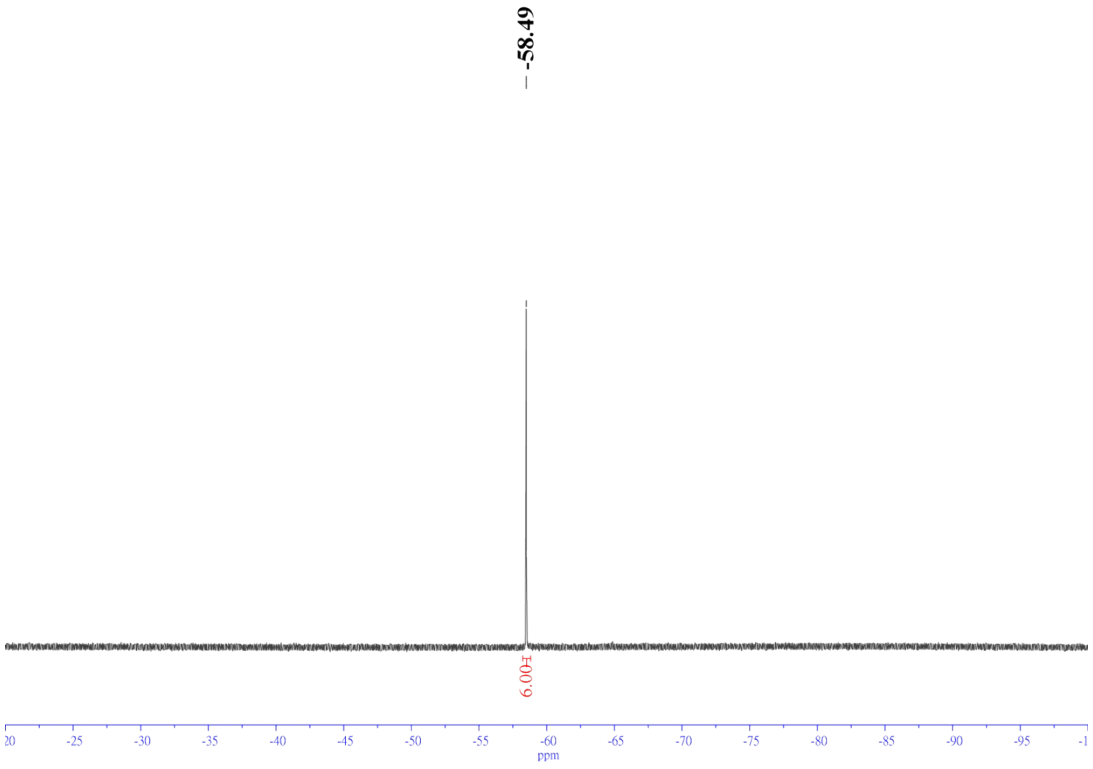

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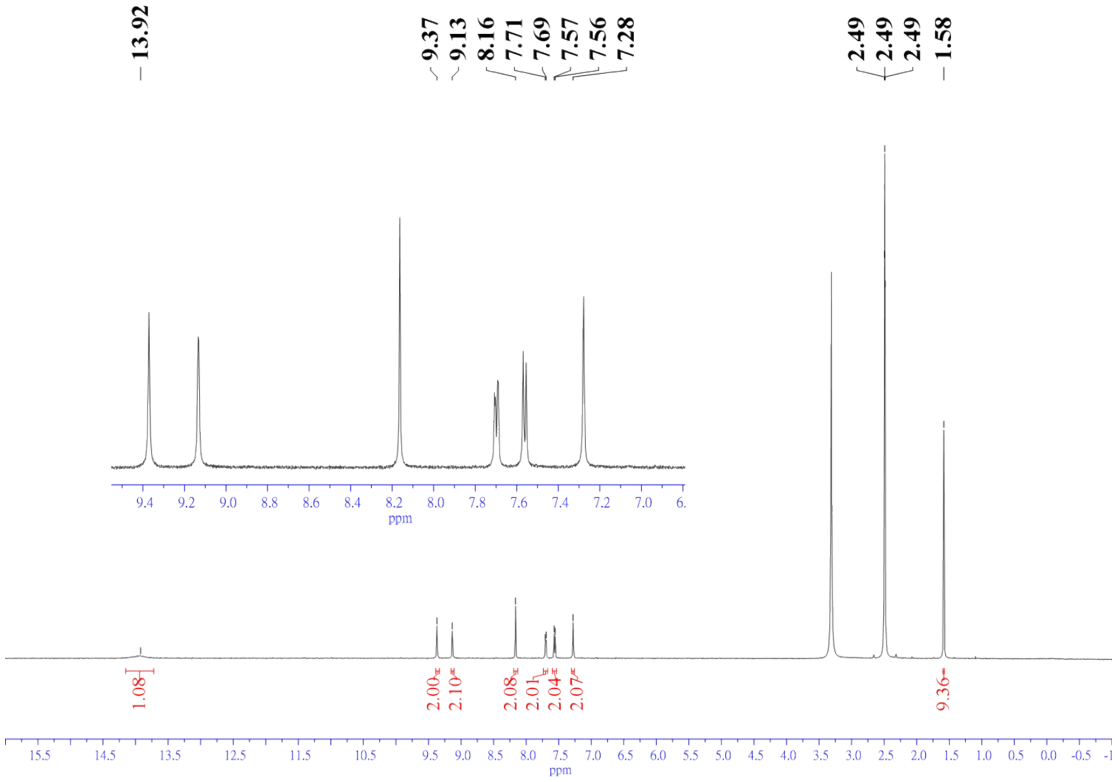
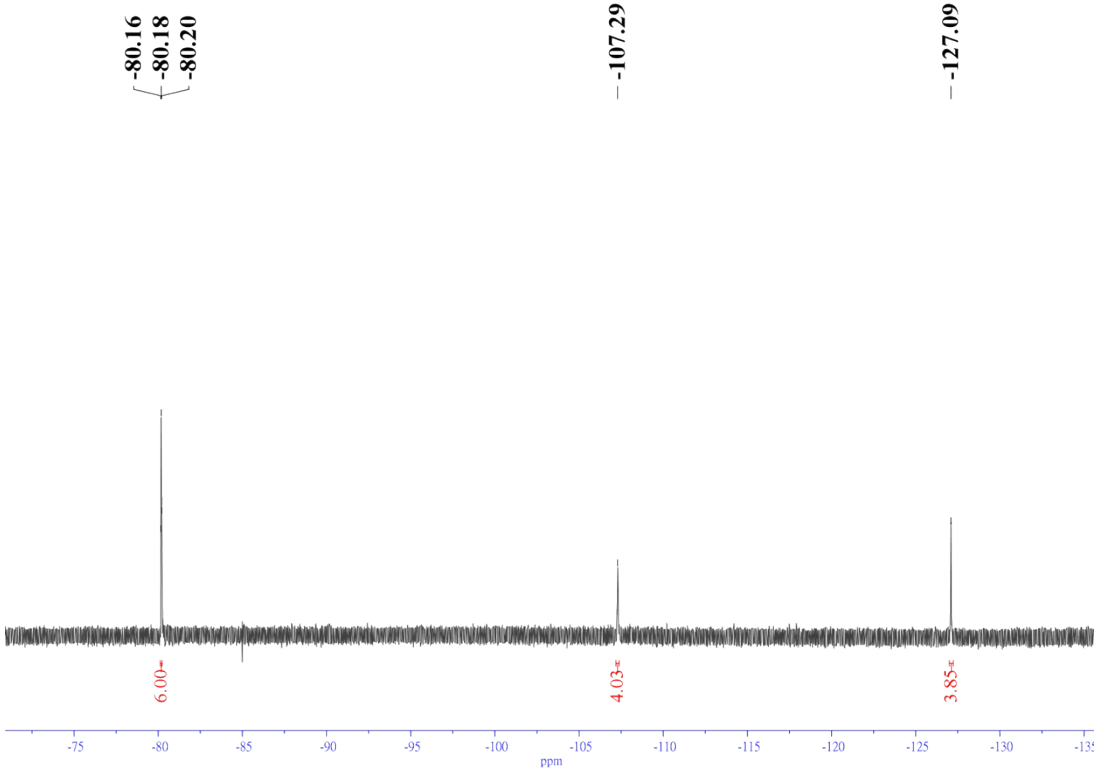
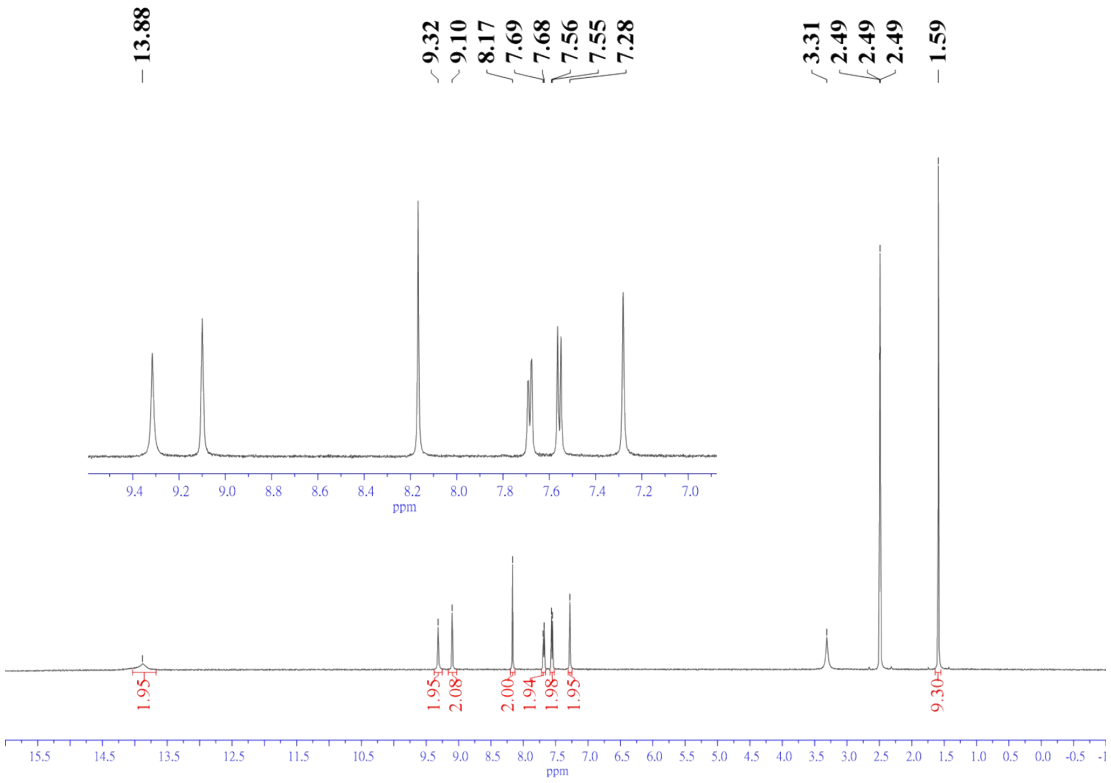


^{19}F NMR spectrum of TF-tBu_C_3F_7 in d_6-DMSO



^{1}H NMR spectrum of TF-tBu_C_5F_{11} in d_6-DMSO



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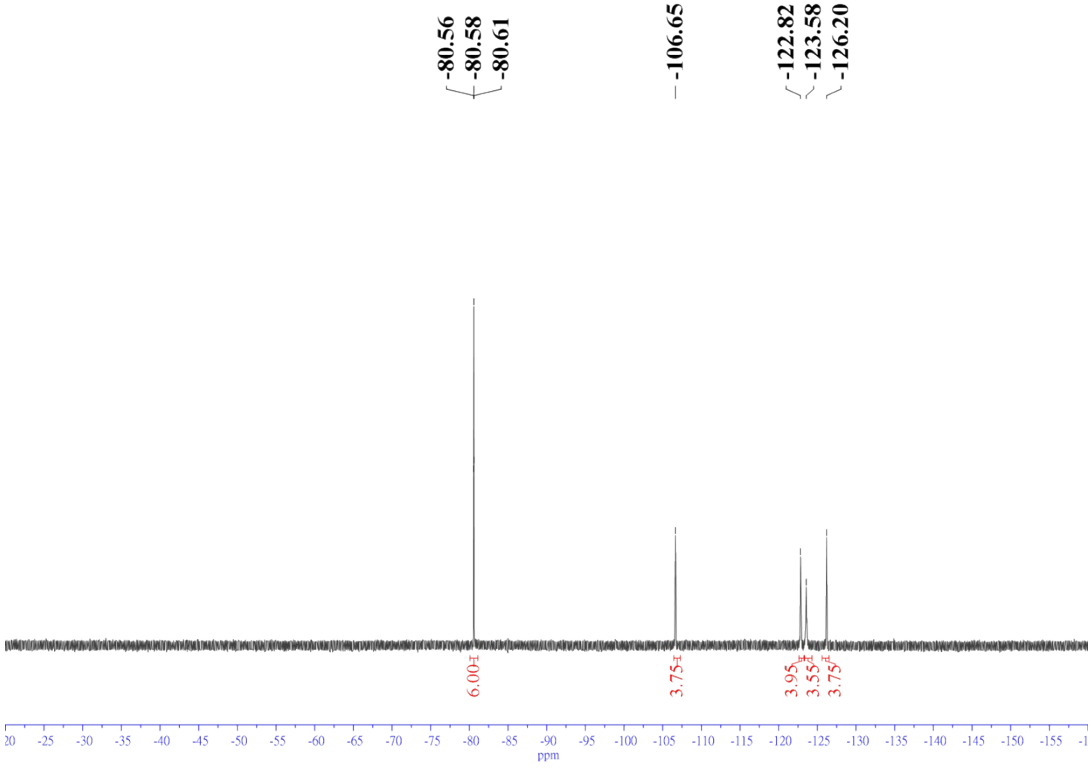

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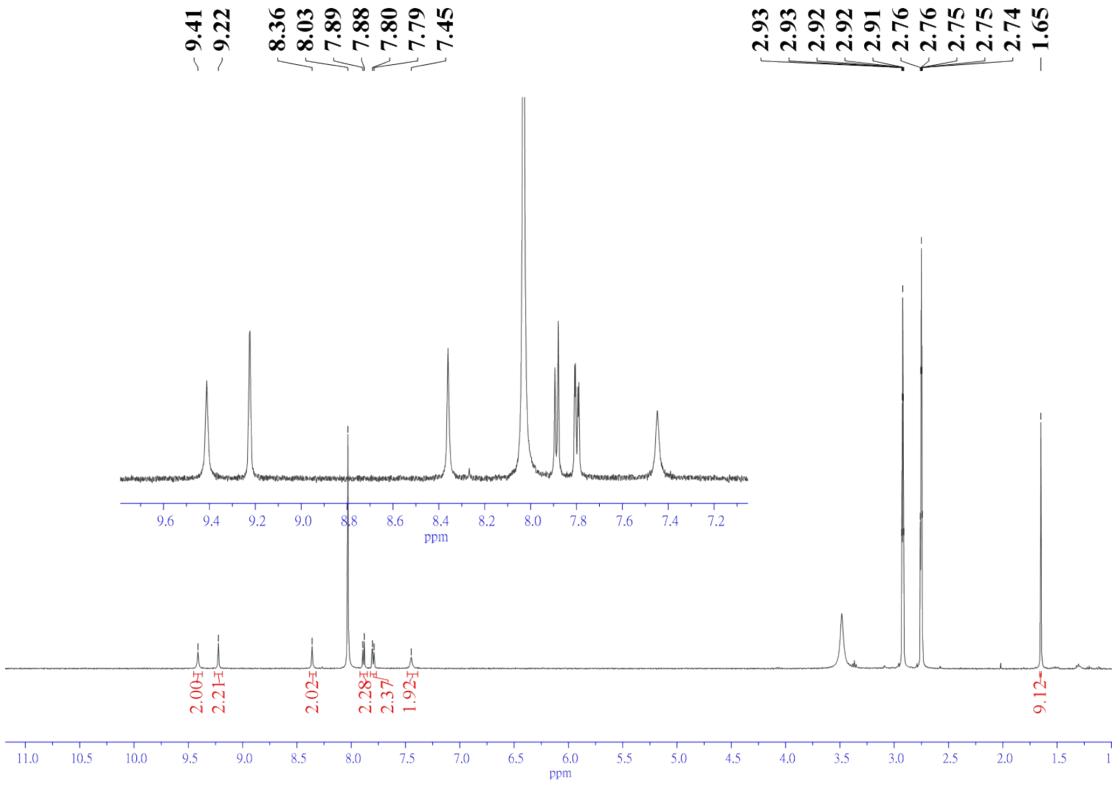

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