

# Trichlorophenyl Formate: Highly Reactive and Easily Accessible Crystalline CO Surrogate for Palladium-Catalyzed Carbonylation of Aryl/Alkenyl Halides and Triflates

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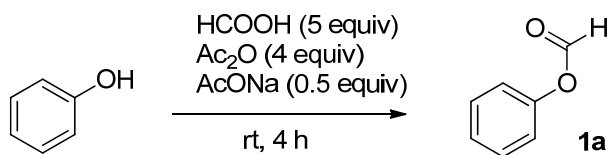
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## **1. General method and materials**

**General.** All reactions were performed in oven-dried or flame-dried glassware under argon atmosphere. Reactions were monitored by TLC on Merck silica gel 60 F254 plates visualized by UV lamp at 254 nm. Column chromatography was performed on Merck silica gel 60 and preparative TLC was performed on Merck silica gel 60 F254 0.5 mm plates. NMR spectra were measured on a JEOL AL-400 NMR spectrometer at 400 MHz for  $^1\text{H}$  spectra and 100 MHz for  $^{13}\text{C}$  spectra. For  $^1\text{H}$  NMR, tetramethylsilane (TMS) ( $\delta = 0$ ) in  $\text{CDCl}_3$  served as an internal standard. For  $^{13}\text{C}$  NMR,  $\text{CDCl}_3$  ( $\delta = 77.0$ ) served as an internal standard. Infrared spectra were measured on a SHIMADZU IR Prestige-21 spectrometer (ATR). High-resolution mass spectra (HRMS) were measured on a JEOL JMS-T100TD time-of-flight mass spectrometer (DART) and JMS-T100GC gas chromatography mass spectrometer. Melting point was measured using a YAZAWA MICRO MELTING POINT BY-1.

**Materials.** Commercially obtained chemicals including Pd catalysts and ligands were purchased from commercial supplier and used as received. All solvents, triethylamine, and tributylamine were purified by distillation prior to use. Spectral data of **18b–d**, **22** were identical to those of commercially available compounds, respectively.

## 2. Representative procedure of the synthesis of phenyl formates (Table 1, entry 1)

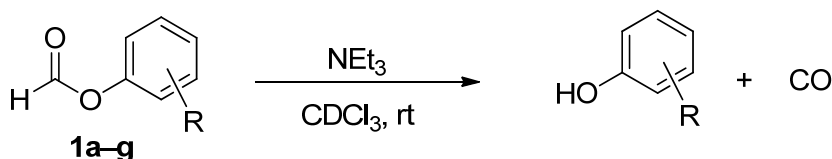


Formic acid (19 mL, 500 mmol, 5.0 equiv) was added to acetic anhydride (38 mL, 400 mmol, 4.0 equiv) at rt. The mixture was stirred at 60 °C for 1 h and cooled to rt. The resulting solution was poured to the flask containing phenol (9.4 g, 100 mmol) and AcONa (4.1 g, 50 mmol, 0.5 equiv). The mixture was stirred for 4 h in water bath and then diluted with toluene (150 mL), washed with H<sub>2</sub>O (100 mL) three times, dried over MgSO<sub>4</sub>, filtered, and concentrated to afford the desired product **1a** (8.7 g, 71 mmol, 71%) as a colorless oil. This product was used for carbonylation reaction without further purification.

### Phenyl formate (**1a**)<sup>1</sup>

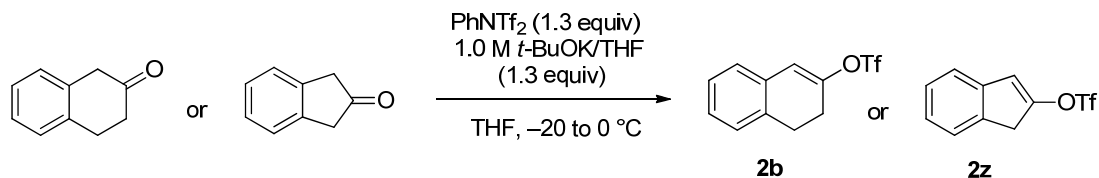
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.28 (s, 1H), 7.39 (ddd, 2H, *J* = 8.3, 7.8, 2.4 Hz), 7.25 (tt, 1H, *J* = 7.8, 1.9 Hz), 7.10 (ddd, 2H, *J* = 8.3, 2.4, 1.9 Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 159.2, 149.8, 129.6, 126.3, and 121.0.

## 3. General procedure of decarbonylation of phenyl formates (Table 1)



NEt<sub>3</sub> (69 μL, 0.50 mmol, 1 equiv) was added to a solution of phenyl formates (**1a-g**, 0.50 mmol) in CDCl<sub>3</sub> (1 mL). The reaction was carried out at rt. The conversion of **1a-g** was analyzed by <sup>1</sup>H-NMR at the suitable interval.

## 4. Representative procedure of the synthesis of alkenyl triflates



The solution of β-tetralone (3.0 g, 21 mmol) in THF (90 mL) was cooled to -20 °C. 1.0 M *t*-BuOK in THF (27 mL, 27 mmol, 1.3 equiv) was added dropwise to the solution over 10 min. The mixture was

warmed to 0 °C, stirred for 1 h, and then cooled to -20 °C. PhNTf<sub>2</sub> (9.5 g, 27 mmol, 1.3 equiv) was added to the solution and the mixture was stirred for 1 h, then warmed to 0 °C, and stirred for 4 h. The mixture was diluted with EtOAc, washed with H<sub>2</sub>O and brine, dried over MgSO<sub>4</sub>, filtered, and concentrated. The obtained residue was purified by silica gel column chromatography (SiO<sub>2</sub>, hexane/EtOAc 200/1) to afford **2b** (4.9 g, 18 mmol, 86%) as a colorless oil.

### 3,4-Dihydronaphthalen-2-yl trifluoromethanesulfonate (**2b**)

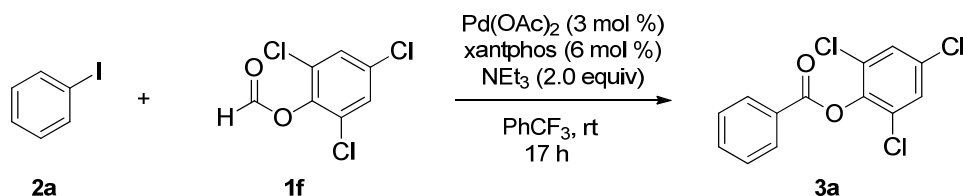
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.21-7.18 (m, 2H), 7.15-7.13 (m, 1H), 7.08-7.05 (m, 1H), 6.48 (s, 1H), 3.05 (t, *J* = 8.4 Hz, 2H), 2.69 (t, *J* = 8.4 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 150.0, 132.9, 131.1, 128.4, 127.5, 127.3, 127.0, 118.6 (q, <sup>1</sup>*J*<sub>CF</sub> = 319.9 Hz), 118.5, 28.5, and 26.5; IR (ATR) 1665, 1416, 1202, 1136, 1063, 986, 895, 824, 752, and 610 cm<sup>-1</sup>; HRMS (TOF) [M+H]<sup>+</sup> calcd for C<sub>11</sub>H<sub>9</sub>F<sub>3</sub>O<sub>3</sub>S: 279.0297; found 279.0291.

### 1*H*-Inden-2-yl trifluoromethanesulfonate (**2z**)

**2z** was obtained from 2-indanone as a colorless oil. Yield: 73%.

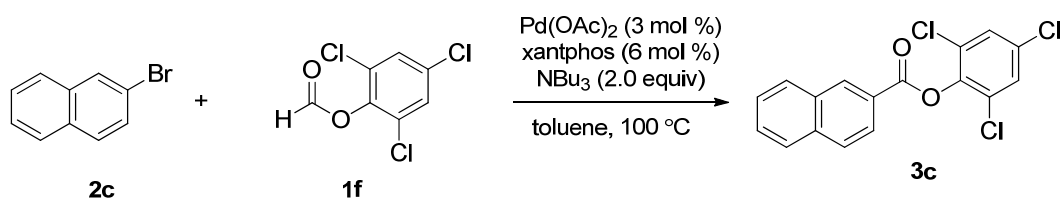
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.38 (m, 2H), 7.31 (t, *J* = 7.2 Hz, 1H), 7.28-7.24 (m, 1H), 6.69 (s, 1H), 3.66 (s, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 153.2, 140.1, 137.3, 127.2, 126.1, 123.8, 122.1, 119.5, 118.6 (q, <sup>1</sup>*J*<sub>CF</sub> = 320.7 Hz), and 37.7; IR (ATR) 1618, 1423, 1244, 1206, 1136, 1103, 1090, 907, 835, 750, and 608 cm<sup>-1</sup>; HRMS (TOF) [M+H]<sup>+</sup> calcd for C<sub>10</sub>H<sub>7</sub>F<sub>3</sub>O<sub>3</sub>S: 265.0141; found 265.0147.

## 5. Representative procedure of room-temperature carbonylation (Method A, Table 2, entry 13)



Pd(OAc)<sub>2</sub> (3.3 mg, 0.015 mmol, 3.0 mol %), xantphos (17.1 mg, 0.029 mmol, 6.0 mol %), and **1f** (221 mg, 0.98 mmol, 2.0 equiv) were added to a 10-mL test tube. The test tube was evacuated and backfilled with argon three times. Then, a degassed solution of iodobenzene (**2a**) (100 mg, 0.490 mmol) in PhCF<sub>3</sub> (0.5 mL) was added to the test tube under flowing argon. The mixture was stirred for 5 min. Right after the addition of degassed NEt<sub>3</sub> (136 μL, 0.98 mmol, 2.0 equiv) to the mixture, the test tube was quickly sealed by a plastic screw cap and the mixture was stirred for 17 h at rt. The reaction mixture was diluted with Et<sub>2</sub>O, filtered, and concentrated. The obtained residue was purified by PTLC (SiO<sub>2</sub>, hexane/EtOAc 10/1) to afford the **3a** (148 mg, 0.49 mmol, >99%) as white crystal.

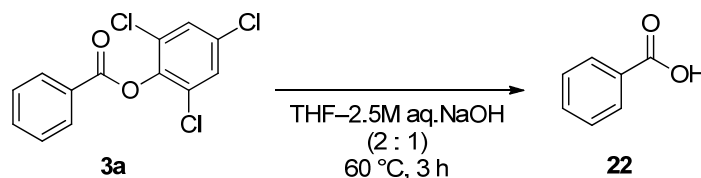
## 6. Representative procedure of the carbonylation of aryl bromides (Method B, Table 3, entry 6)



$\text{Pd}(\text{OAc})_2$  (33 mg, 0.15 mmol, 3.0 mol %), xantphos (168 mg, 0.29 mmol, 6.0 mol %), and 2-bromonaphthalene (**2c**) (1.00 g, 4.83 mmol) were added to a 50-mL flask. The flask was evacuated and backfilled with argon three times. Then, a degassed solution of  $\text{NBu}_3$  (2.3 mL, 9.7 mmol, 2.0 equiv) in toluene (5 mL) was added to the flask equipped with argon balloon. The mixture was warmed to 100 °C and stirred for 5 min. The degassed solution of **1f** (1.3 g, 5.8 mmol, 1.2 equiv) in toluene (9 mL) was added to the mixture over 3 h with syringe pump. After additional stirring at 100 °C for 1 h, the mixture was cooled to rt and concentrated. The obtained residue was purified by silica gel column chromatography ( $\text{SiO}_2$ , hexane/EtOAc 100/1) to afford **3c** (1.5 g, 4.3 mmol, 89%) as a white crystal.

## 7. Transformation of 2,4,6-trichlorophenyl ester (**3a**) (Scheme 2)

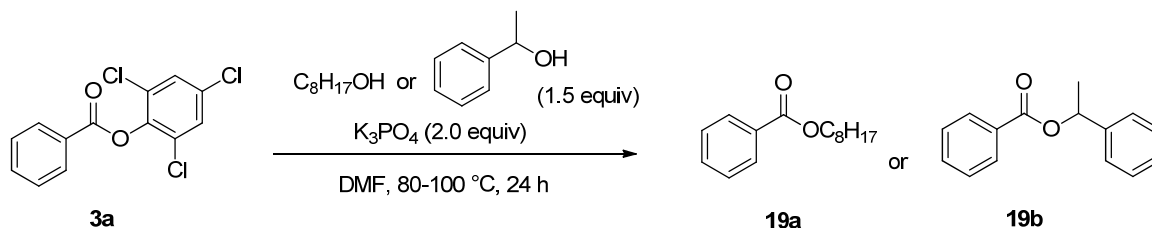
### 7.1. Synthesis of benzoic acid (**22**)



To a solution of **3a** (100 mg, 0.332 mmol) in THF (1 mL) was added 2.5 M aq. NaOH (0.5 mL). The mixture was warmed to 60 °C, stirred for 3 h, and cooled to rt. After the addition of 1 M aq. HCl, the mixture was extracted with  $\text{CH}_2\text{Cl}_2$  twice. The combined organic layer was dried over  $\text{MgSO}_4$ , filtered, and concentrated. The obtained residue was purified by PTLC ( $\text{SiO}_2$ , hexane/EtOAc 1/1) to afford **22** (38 mg, 0.31 mmol, 94%) as a white crystal (m.p. 122 °C).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  11.09 (brs, 1H), 8.12 (d,  $J$  = 7.6 Hz, 2H), 7.61 (t,  $J$  = 7.6 Hz, 1H), 7.48 (t,  $J$  = 7.6 Hz, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  172.4, 133.8, 130.2, 129.3, and 128.5.

## 7.2. Representative procedure of esterification



$K_3PO_4$  (141 mg, 0.66 mmol, 2.0 equiv) was added to a solution of **3a** (100 mg, 0.33 mmol) and *n*-octanol (79  $\mu$ L, 0.50 mmol, 1.5 equiv) in DMF (1 mL). The mixture was warmed to 100 °C, stirred for 24 h, and cooled to rt. The mixture was diluted with EtOAc, filtered, and concentrated. The obtained residue was purified by PTLC ( $SiO_2$ , hexane/EtOAc 10/1) to afford **19a** (65 mg, 0.28 mmol, 84%) as a colorless oil.

### *n*-Octyl benzoate (**19a**)<sup>2</sup>

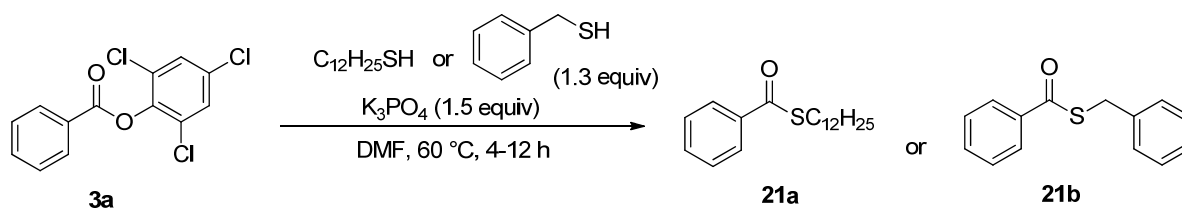
$^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  8.05 (d,  $J$  = 7.8 Hz, 2H), 7.55 (t,  $J$  = 7.8 Hz, 1H), 7.44 (t,  $J$  = 7.8 Hz, 2H), 4.32 (t,  $J$  = 6.9 Hz, 2H), 1.80–1.73 (m, 2H), 1.48–1.41 (m, 2H), 1.34–1.28 (m, 8H), 0.88 (t,  $J$  = 6.9 Hz, 3H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  166.7, 132.8, 130.5, 129.5, 128.3, 65.1, 31.8, 29.24, 29.18, 28.7, 26.0, 22.6, and 14.0.

### 1-Phenylethyl benzoate (**19b**)<sup>3</sup>

**19b** was obtained from **3a** and 1-phenylethyl alcohol as a colorless oil. The reaction was conducted at 80 °C for 24 h. Yield: 84%.

$^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  8.07 (d,  $J$  = 7.5 Hz, 2H), 7.55 (t,  $J$  = 7.5 Hz, 1H), 7.44–7.41 (m, 4H), 7.36 (t,  $J$  = 7.5 Hz, 2H), 7.29 (t,  $J$  = 7.3 Hz, 1H), 6.13 (q,  $J$  = 6.6 Hz, 1H), 1.67 (d,  $J$  = 6.6 Hz, 3H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  165.7, 141.7, 132.9, 130.5, 129.6, 128.5, 128.3, 127.8, 126.0, 72.9, and 22.4.

## 7.3. Representative procedure of thioesterification



$K_3PO_4$  (106 mg, 0.50 mmol, 1.5 equiv) was added to a solution of **3a** (100 mg, 0.33 mmol) and 1-dodecyl mercaptan (103  $\mu$ L, 0.43 mmol, 1.3 equiv) in DMF (1 mL). The mixture was warmed to 60 °C, stirred for 12 h, and cooled to rt. The mixture was directly purified by PTLC ( $SiO_2$ , hexane/EtOAc 20/1) to afford **21a** (96 mg, 0.31 mmol, 94%) as a colorless oil.

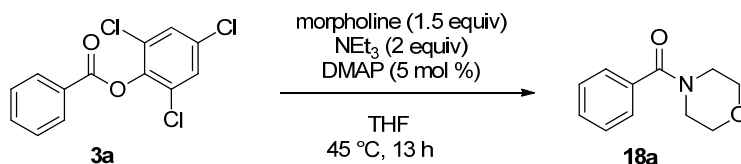
**Dodecyl benzothioate (21a)**<sup>4</sup>

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.96 (d, *J* = 8.0 Hz, 2H), 7.54 (t, *J* = 8.0 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 3.06 (t, *J* = 7.6 Hz, 2H), 1.72-1.65 (m, 2H), 1.49-1.35 (m, 2H), 1.35-1.20 (m, 16H), 0.88 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 192.0, 137.3, 133.1, 128.5, 127.1, 31.9, 29.61, 29.60, 29.56, 29.54, 29.47, 29.3, 29.1, 29.0, 28.9, 22.7, and 14.1.

**Benzyl benzothioate (21b)**<sup>5</sup>

**21b** was obtained from **3a** and benzyl mercaptan as a colorless oil. The reaction time was 4 h. Yield: 95%.

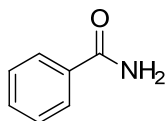
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.98-7.96 (m, 2H), 7.58-7.54 (m, 1H), 7.46-7.42 (m, 2H), 7.39-7.37 (m, 2H), 7.33-7.30 (m, 2H), 7.27-7.24 (m, 1H), 4.32 (s, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 191.3, 137.5, 136.8, 133.5, 129.0, 128.7, 128.6, 128.5, 127.3, 127.2, and 33.4.

**7.4. Representative procedure of amidation**

Morpholine (44 μL, 0.50 mmol, 1.5 equiv) and DMAP (2.0 mg, 0.017 mmol, 0.05 equiv) were added to a solution of **3a** (100 mg, 0.33 mmol) and NEt<sub>3</sub> (92 μL, 0.66 mmol, 2.0 equiv) in THF (1 mL). The mixture was warmed to 45 °C, stirred for 13 h, and cooled to rt. The mixture was concentrated and directly purified by PTLC (SiO<sub>2</sub>, hexane/EtOAc 1/1) to afford **18a** (62 mg, 0.33 mmol, 98%) as a white crystal (m.p. 73 °C).

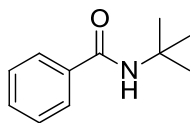
**Morpholino(phenyl)methanone (18a)**<sup>6</sup>

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.41 (brs, 5H), 3.72 (brs, 8H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 170.3, 135.2, 129.7, 128.4, 127.9, 127.0, and 66.8.

**Benzamide (18b)**

**18b** was obtained from **3a** and 3 equiv of 0.5 M NH<sub>3</sub>/dioxane as a white solid (m.p. 125 °C). The reaction time was 13 h. Yield: 98%.

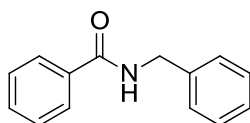
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.82 (d, *J* = 8.4 Hz, 2H), 7.53 (t, *J* = 7.6 Hz, 1H), 7.44 (dd, *J* = 8.4, 7.6 Hz, 2H), 6.29 (brs, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 169.7, 133.4, 131.9, 128.6, and 127.3.



#### ***N*-tert-Butylbenzamide (18c)**

**18c** was obtained from **3a** and 2 equiv of *tert*-butylamine as a white solid (m.p. 136 °C). The reaction was conducted at 60 °C for 21 h. Yield: 99%.

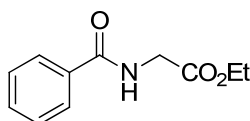
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.73-7.69 (m, 2H), 7.48-7.35 (m, 3H), 6.01 (brs, 1H), 1.47 (s, 9H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 166.9, 135.9, 131.0, 128.4, 126.6, 51.5, and 28.8.



#### ***N*-benzylbenzamide (18d)**

**18d** was obtained from **3a** and benzylamine as a white solid (m.p. 104 °C). The reaction time was 13 h. Yield: 97%.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.80-7.75 (m, 2H), 7.48-7.43 (m, 1H), 7.38-7.21 (m, 7H), 6.82 (brs, 1H), 4.57 (d, *J* = 5.6 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 167.4, 138.2, 134.3, 131.4, 128.6, 128.4, 127.7, 127.4, 127.3, 126.9, and 43.9.

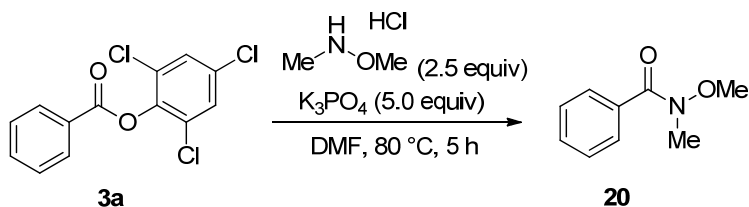


#### **Ethyl-2-benzamidoacetate (18e)<sup>7</sup>**

**18e** was obtained from **3a** and glycine ethyl ester hydrochloride as a white solid (m.p. 61 °C). The reaction time was 13 h. Yield: 97%.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.82 (d, *J* = 8.0 Hz, 2H), 7.49 (t, *J* = 6.8 Hz, 1H), 7.41 (dd, *J* = 8.0, 6.8 Hz, 2H), 6.79 (br, 1H), 4.28-4.20 (m, 4H), 1.31 (t, *J* = 7.0 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 170.0, 167.5, 133.6, 131.6, 128.5, 127.0, 61.5, 41.8, and 14.0.

### **7.5. Synthesis of *N*-methoxyl-*N*-methylbenzamide (**20**)<sup>8</sup>**

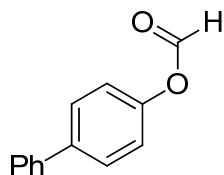


K<sub>3</sub>PO<sub>4</sub> (352 mg, 1.66 mmol, 5 equiv) and *N,O*-dimethylhydroxylamine hydrochloride (81 mg, 0.83 mmol, 2.5 equiv) was added to a solution of **3a** (100 mg, 0.33 mmol) in DMF (1 mL). The mixture was warmed to 80 °C, stirred for 5 h, and cooled to room temperature. The mixture was diluted with EtOAc, filtered, and concentrated. The obtained residue was purified by PTLC (SiO<sub>2</sub>, hexane/EtOAc 4/1) to afford **20** (48 mg, 0.29 mmol, 87%) as a colorless oil.



$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.66-7.64 (m, 2H), 7.46-7.35 (m, 3H), 3.55 (s, 3H), 3.36 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  169.9, 134.1, 130.5, 128.1, 128.0, 61.0, and 33.8.

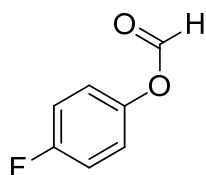
#### **8. Analytical data of phenyl formates (1b–g)**



##### **4-Phenylphenyl formate (1b)<sup>9</sup>**

**1b** was obtained from 4-phenylphenol as a white crystal (m.p. 58 °C). 8 equiv of  $\text{Ac}_2\text{O}$ , 10 equiv of  $\text{HCOOH}$ , and 1 equiv of  $\text{AcONa}$  were used. Yield: 96%.

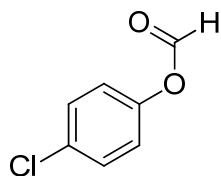
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.34 (s, 1H), 7.63-7.54 (m, 5H), 7.46-7.42 (m, 2H), 7.38-7.33 (m, 1H), 7.22-7.18 (m, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  159.2, 149.2, 140.1, 139.6, 128.8, 128.4, 127.5, 127.1, and 121.4; IR (ATR) 1726, 1599, 1518, 1483, 1217, 1184, 1169, 1098, 858, 750, and 685  $\text{cm}^{-1}$ ; HRMS (TOF)  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{13}\text{H}_{10}\text{O}_2$ : 199.0754; found 199.0753.



##### **4-Fluorophenyl formate (1c)<sup>10</sup>**

**1c** was obtained from 4-fluorophenol as a colorless oil. Yield: 66%.

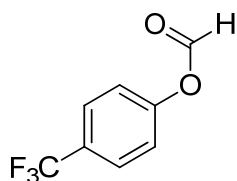
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.28 (s, 1H), 7.14-7.04 (m, 4H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  160.5 (d,  $^1J_{\text{CF}} = 244.7$  Hz), 159.1, 145.6 (d,  $^4J_{\text{CF}} = 3.3$  Hz), 122.6 (d,  $^3J_{\text{CF}} = 8.8$  Hz), 116.3 (d,  $^2J_{\text{CF}} = 23.2$  Hz); IR (ATR) 1763, 1736, 1499, 1180, 1090, 862, 793, and 704  $\text{cm}^{-1}$ ; HRMS (TOF)  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_7\text{H}_5\text{FO}_2$ : 141.0346; found 141.0356.



##### **4-Chlorophenyl formate (1d)<sup>9</sup>**

**1d** was obtained from 4-chlorophenol as a colorless oil. Yield: 95%.

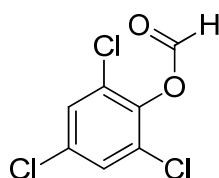
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.26 (s, 1H), 7.35 (d,  $J = 8.8$  Hz, 2H), 7.07 (d,  $J = 8.8$  Hz, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  158.7, 148.2, 131.7, 129.6, and 122.5; IR (ATR) 1763, 1741, 1485, 1190, 1163, 1105, 1082, 860, 777, 611, and 513  $\text{cm}^{-1}$ ; HRMS (TOF)  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_7\text{H}_5\text{ClO}_2$ : 157.0051; found 157.0057.



#### 4-Trifluoromethylphenyl formate (**1e**)<sup>10</sup>

**1e** was obtained from 4-trifluoromethylphenol as a colorless oil. Yield: 91%.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.31 (s, 1H), 7.68 (d, *J* = 8.8 Hz, 2H), 7.28 (d, *J* = 8.8 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 158.5, 152.3, 128.7 (q, <sup>2</sup>*J*<sub>CF</sub> = 33.0 Hz), 127.1 (q, <sup>3</sup>*J*<sub>CF</sub> = 3.7 Hz), 123.8 (q, <sup>1</sup>*J*<sub>CF</sub> = 272.0 Hz), and 121.8; IR (ATR) 1770, 1744, 1612, 1512, 1323, 1202, 1167, 1120, 1099, 1059, 1016, 870, 737, 594, and 571 cm<sup>-1</sup>; HRMS (CI) [M+H]<sup>+</sup> calcd for C<sub>8</sub>H<sub>5</sub>F<sub>3</sub>O<sub>2</sub>: 191.0314; found 191.0320.



#### 2,4,6-Trichlorophenyl formate (**1f**)<sup>11</sup>

**1f** was obtained from 2,4,6-trichlorophenol as a pale yellow crystal (m.p. 68 °C). 8 equiv of Ac<sub>2</sub>O, 10 equiv of HCOOH, and 1 equiv of AcONa were used. Yield: 98%.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.28 (s, 1H), 7.40 (s, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 156.2, 141.9, 132.5, 129.2, and 128.7; IR (ATR) 3078, 1732, 1562, 1447, 1418, 1385, 1368, 1227, 1084, 1055, 849, 818, 804, 687, and 561 cm<sup>-1</sup>; HRMS (CI) [M+H]<sup>+</sup> calcd for C<sub>7</sub>H<sub>3</sub>Cl<sub>3</sub>O<sub>2</sub>: 224.9271; found 224.9279.

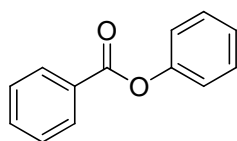


#### 2,6-Difluorophenyl formate (**1g**)

**1g** was obtained from 2,6-difluorophenol as a colorless oil. Yield: 53%.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.28 (s, 1H), 7.26-7.16 (m, 1H), 7.03-6.96 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 156.7, 155.0 (dd, <sup>1,3</sup>*J*<sub>CF</sub> = 251.2, 4.1 Hz), 126.0 (t, <sup>2</sup>*J*<sub>CF</sub> = 15.7 Hz), 126.9 (t, <sup>3</sup>*J*<sub>CF</sub> = 9.0 Hz), and 112.2 (dd, <sup>2,4</sup>*J*<sub>CF</sub> = 17.3, 5.0 Hz); IR (ATR) 1748, 1612, 1493, 1477, 1292, 1248, 1196, 1076, 1011, 770, and 694 cm<sup>-1</sup>; HRMS (CI) [M+H]<sup>+</sup> calcd for C<sub>7</sub>H<sub>4</sub>F<sub>2</sub>O<sub>2</sub>: 159.0252; found 159.0259.

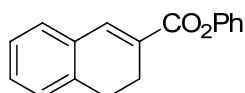
### 9. Analytical data of carbonylation products



#### Phenyl benzoate (**6**)<sup>1</sup>

**6** was obtained from **1a** and **2a** as a white crystal (m.p. 68 °C) by method A. Yield: 10%.

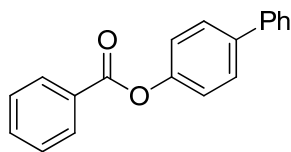
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.21 (ddd, *J* = 7.3, 2.0, 1.0 Hz, 2H), 7.62 (tt, *J* = 7.3, 2.0 Hz, 1H), 7.50 (ddd, *J* = 7.8, 7.8, 1.0 Hz, 2H), 7.42 (ddd, *J* = 7.3, 7.3, 1.0 Hz, 2H), 7.26 (tt, *J* = 7.8, 1.4 Hz, 1H), 7.21 (ddd, *J* = 7.8, 1.4, 1.0 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 165.1, 150.9, 133.5, 130.1, 129.5, 129.4, 128.5, 125.8, and 121.7.



**Phenyl 3,4-dihydronaphthalene-2-carboxylate (7)**<sup>12</sup>

**7** was obtained from **1a** and **2b** as a white crystal (m.p. 55 °C) by method A. Yield: 30%.

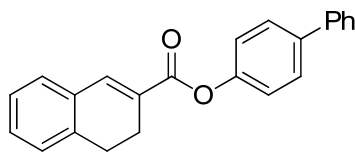
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.76 (s, 1H), 7.40 (t, *J* = 7.8 Hz, 2H), 7.30-7.15 (m, 7H), 2.93 (t, *J* = 8.3 Hz, 2H), 2.72 (t, *J* = 8.3 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 165.8, 151.0, 138.2, 137.1, 132.3, 129.9, 129.4, 128.7, 128.6, 127.7, 126.8, 125.6, 121.7, 27.5, and 22.3; IR (ATR) 1721, 1626, 1566, 1481, 1450, 1260, 1186, 1161, 1109, 1049, 734, and 689 cm<sup>-1</sup>; HRMS (TOF) [M+H]<sup>+</sup> calcd for C<sub>17</sub>H<sub>15</sub>O<sub>2</sub>: 251.1066; found 251.1074.



**4-Phenylphenyl benzoate (8)**

**8** was obtained from **1b** and **2a** as a white crystal (m.p. 139 °C) by method A. Yield: 5%.

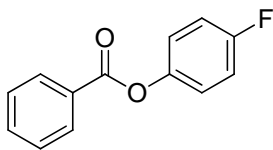
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.22 (d, *J* = 7.6 Hz, 2H), 7.66-7.55 (m, 5H), 7.52 (t, *J* = 7.6 Hz, 2H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.37-7.32 (m, 1H), 7.29 (d, *J* = 8.8 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 165.2, 150.4, 140.4, 139.0, 133.6, 130.2, 129.6, 128.8, 128.6, 128.2, 127.3, 127.1, and 122.0; IR (ATR) 1730, 1597, 1485, 1450, 1402, 1263, 1230, 1217, 1167, 1063, 878, 756, 700, and 687 cm<sup>-1</sup>; HRMS (TOF) [M+H]<sup>+</sup> calcd for C<sub>19</sub>H<sub>14</sub>O<sub>2</sub>: 275.1067; found 275.1071.



**1,1'-Biphenyl-4-yl 3,4-dihydronaphthalene-2-carboxylate (9)**

**9** was obtained from **1b** and **2b** as a white crystal (m.p. 113 °C) by method A. Yield: 17%.

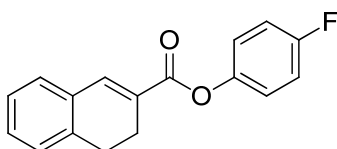
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.79 (s, 1H), 7.62 (d, *J* = 8.4 Hz, 2H), 7.58 (d, *J* = 8.4 Hz, 2H), 7.44 (t, *J* = 7.2 Hz, 2H), 7.37-7.20 (m, 7H), 2.95 (t, *J* = 8.4 Hz, 2H), 2.75 (t, *J* = 8.4 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 165.9, 150.5, 140.4, 138.8, 138.4, 137.1, 132.3, 129.9, 128.8, 128.6, 128.2, 127.8, 127.3, 127.1, 126.8, 122.0, 27.6, and 22.3 (One aromatic carbon signal is missing.); IR (ATR) 1732, 1624, 1564, 1447, 1379, 1275, 1238, 1200, 1182, 1167, 1134, 1109, 1022, 959, 906, 854, 817, and 729 cm<sup>-1</sup>; HRMS (TOF) [M+H]<sup>+</sup> calcd for C<sub>23</sub>H<sub>18</sub>O<sub>2</sub>: 327.1380; found 327.1386.



#### 4-Fluorophenyl benzoate (10)

**10** was obtained from **1c** and **2a** as a white crystal (m.p. 49 °C) by method A. Yield: 30%.

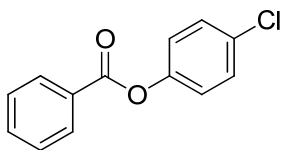
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.21-8.18 (m, 2H), 7.64 (tt,  $J = 7.6, 2.0$  Hz, 1H), 7.52 (t,  $J = 7.5$  Hz, 2H), 7.20-7.15 (m, 2H), 7.14-7.08 (m, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  165.2, 160.3 (d,  $^1J_{\text{CF}} = 243.8$  Hz), 146.7, 133.7, 130.2, 129.3, 128.6, 123.1 (d,  $^3J_{\text{CF}} = 8.2$  Hz), 116.1 (d,  $^2J_{\text{CF}} = 23.9$  Hz); IR (ATR) 1730, 1599, 1499, 1450, 1267, 1240, 1184, 1061, 1024, 1012, 876, 818, 763, and 698  $\text{cm}^{-1}$ ; HRMS (TOF)  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{13}\text{H}_9\text{FO}_2$ : 217.0659; found 217.0662.



#### 4-Fluorophenyl 3,4-dihydronaphthalene-2-carboxylate (11)

**11** was obtained from **1c** and **2b** as a colorless oil by method A. Yield: 35%.

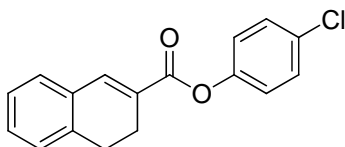
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.75 (s, 1H), 7.29-7.19 (m, 4H), 7.16-7.05 (m, 4H), 2.93 (t,  $J = 8.4$  Hz, 2H), 2.71 (td,  $J = 8.4, 1.2$  Hz, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  165.9, 160.1 (d,  $^1J_{\text{CF}} = 243.8$  Hz), 146.8 (d,  $^4J_{\text{CF}} = 2.5$  Hz), 138.5, 137.1, 132.2, 130.0, 128.8, 128.3, 127.8, 126.8, 123.0 (d,  $^3J_{\text{CF}} = 8.2$  Hz), 116.0 (d,  $^2J_{\text{CF}} = 23.1$  Hz), 27.5, and 22.3; IR (ATR) 1717, 1624, 1501, 1275, 1260, 1204, 1173, 1148, 1110, 1047, 968, 831, 758, 746, and 718  $\text{cm}^{-1}$ ; HRMS (TOF)  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{17}\text{H}_{13}\text{FO}_2$ : 269.0972; found 269.0980.



#### 4-Chlorophenyl benzoate (12)

**12** was obtained from **1d** and **2a** as a white crystal (m.p. 72 °C) by method A. Yield: 81%.

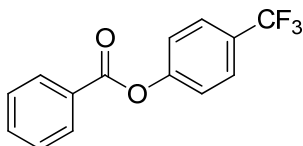
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.18 (dd,  $J = 7.6, 1.6$  Hz, 2H), 7.63 (tt, 1H,  $J = 8.0, 1.6$  Hz, 1H), 7.50 (dd,  $J = 8.0, 7.6$  Hz, 2H), 7.37 (d,  $J = 8.8$  Hz, 2H), 7.16 (d,  $J = 8.8$  Hz, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  164.9, 149.4, 133.7, 131.2, 130.2, 129.5, 129.1, 128.6, and 123.1; IR (ATR) 1730, 1485, 1450, 1261, 1215, 1200, 1159, 1078, 1059, 1024, 1013, 1001, 876, 806, 799, 702, and 683  $\text{cm}^{-1}$ ; HRMS (TOF)  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{13}\text{H}_9\text{ClO}_2$ : 233.0364; found 233.0360.



#### 4-Chlorophenyl 3,4-dihydronaphthalene-2-carboxylate (**13**)

**13** was obtained from **1d** and **2b** as a white crystal (m.p. 67 °C) by method A. Yield: 87%.

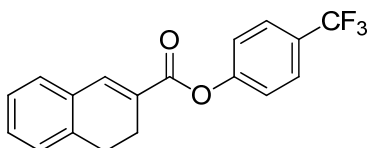
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.74 (s, 1H), 7.37-7.33 (m, 2H), 7.30-7.18 (m, 4H), 7.13-7.09 (m, 2H), 2.92 (t,  $J = 8.4$  Hz, 2H), 2.70 (td,  $J = 8.4, 1.2$  Hz, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  165.5, 149.5, 138.6, 137.1, 132.2, 130.9, 130.0, 129.4, 128.8, 128.2, 127.7, 126.8, 123.1, 27.5, and 22.2; IR (ATR) 1732, 1719, 1618, 1481, 1258, 1159, 1085, 1045, 1012, 877, 770, and 716  $\text{cm}^{-1}$ ; HRMS (TOF)  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{17}\text{H}_{13}\text{ClO}_2$ : 285.0677; found 285.0673.



#### 4-Trifluoromethylphenyl benzoate (**14**)

**14** was obtained from **1e** and **2a** as a white crystal (m.p. 96 °C) by method A. Yield: 94%.

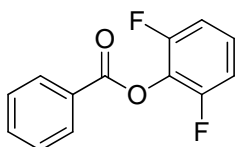
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.20 (dd,  $J = 8.4, 1.2$  Hz, 2H), 7.68 (d,  $J = 8.4$  Hz, 2H), 7.66-7.62 (m, 1H), 7.51 (t,  $J = 8.0$  Hz, 2H), 7.34 (d,  $J = 8.4$  Hz, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  164.6, 153.5, 133.9, 130.2, 128.9, 128.7, 128.1 (q,  $^2J_{\text{CF}} = 33.0$  Hz), 126.8 (q,  $^3J_{\text{CF}} = 3.2$  Hz), 123.9 (q,  $^1J_{\text{CF}} = 272.0$  Hz), and 122.2; IR (ATR) 1732, 1610, 1599, 1516, 1452, 1333, 1261, 1225, 1207, 1157, 1115, 1099, 1051, 881, 702, and 683  $\text{cm}^{-1}$ ; HRMS (TOF)  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{14}\text{H}_9\text{F}_3\text{O}_2$ : 267.0627; found 267.0623.



#### 4-Trifluoromethylphenyl 3,4-dihydronaphthalene-2-carboxylate (**15**)

**15** was obtained from **1e** and **2b** as a white crystal (m.p. 103 °C) by method A. Yield: 91%.

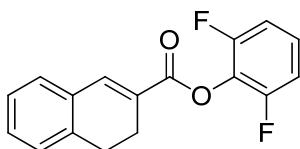
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.78 (s 1H), 7.66 (d,  $J = 8.8$  Hz, 2H), 7.31-7.19 (m, 6H), 2.94 (t,  $J = 8.0$  Hz, 2H), 2.72 (t,  $J = 8.0$  Hz, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  165.3, 153.6, 139.0, 137.2, 132.1, 130.2, 128.9, 128.0, 127.9 (q,  $^2J_{\text{CF}} = 33.1$  Hz), 127.8, 126.9, 126.7 (q,  $^3J_{\text{CF}} = 4.1$  Hz), 123.9 (q,  $^1J_{\text{CF}} = 272.0$  Hz), 122.2, 27.5, and 22.2; IR (ATR) 1724, 1622, 1611, 1327, 1260, 1215, 1163, 1101, 1066, 1042, 1016, 984, 953, 880, 862, 762, and 716  $\text{cm}^{-1}$ ; HRMS (TOF)  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{18}\text{H}_{13}\text{F}_3\text{O}_2$ : 319.0940; found 319.0931.



### 2,6-Difluorophenyl benzoate (16)

**16** was obtained from **1g** and **2a** as a colorless oil by method A. Yield: 99%.

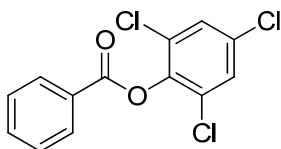
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.22 (dd,  $J = 8.4, 1.2$  Hz, 2H), 7.65 (tt,  $J = 7.6, 1.2$  Hz, 1H), 7.52 (t,  $J = 8.4$  Hz, 2H), 7.24-7.16 (m, 1H), 7.04-6.99 (m, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  163.3, 155.5 (dd,  $^1, ^3J_{\text{CF}} = 250.4, 4.1$  Hz), 134.1, 130.5, 128.7, 128.0, 127.5 (t,  $^2J_{\text{CF}} = 14.9$  Hz), 126.4 (t,  $^3J_{\text{CF}} = 9.1$  Hz), and 112.1 (dd,  $^2, ^4J_{\text{CF}} = 17.4, 4.9$  Hz); IR (ATR) 1749, 1605, 1501, 1479, 1452, 1292, 1258, 1246, 1202, 1179, 1076, 1045, 1011, 772, 702, 685, 520 and 513  $\text{cm}^{-1}$ ; HRMS (TOF)  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{13}\text{H}_8\text{F}_2\text{O}_2$ : 235.0565; found 235.0569.



### 2,6-Difluorophenyl 3,4-dihydronaphthalene-2-carboxylate (17)

**17** was obtained from **1g** and **2b** as a colorless oil by method A. Yield: 94%.

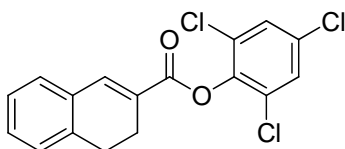
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.83 (s, 1H), 7.30-7.15 (m, 5H), 7.00 (t,  $J = 8.0$  Hz, 2H), 2.95 (t,  $J = 8.4$  Hz, 2H), 2.74 (td,  $J = 8.4, 1.6$  Hz, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  163.9, 155.6 (dd,  $^1, ^3J_{\text{CF}} = 250.5, 4.2$  Hz), 139.7, 137.2, 132.1, 130.2, 129.0, 127.8, 127.6 (t,  $^2J_{\text{CF}} = 15.7$  Hz), 126.9, 126.8, 126.1 (t,  $^3J_{\text{CF}} = 9.1$  Hz), 112.0 (dd,  $^2, ^4J_{\text{CF}} = 17.3, 5.7$  Hz), 27.4, and 22.3; IR (ATR) 1730, 1622, 1599, 1501, 1477, 1292, 1275, 1260, 1246, 1200, 1165, 1155, 1109, 1011, 959, 770, 752, and 714  $\text{cm}^{-1}$ ; HRMS (TOF)  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{17}\text{H}_{12}\text{F}_2\text{O}_2$ : 287.0878; found 287.0869.



### 2,4,6-Trichlorophenyl benzoate (3a)

**3a** was obtained from **1f** and **2a** as a white crystal (m.p. 55  $^{\circ}\text{C}$ ) by method A. Yield: >99%.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.23 (dd,  $J = 8.0, 1.2$  Hz, 2H), 7.66 (tt,  $J = 7.2, 1.2$  Hz, 1H), 7.53 (dd,  $J = 8.0, 7.2$  Hz, 2H), 7.41 (s, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  162.9, 143.2, 134.2, 132.0, 130.5, 129.8, 128.7, 128.6, and 127.8; IR (ATR) 1753, 1447, 1258, 1227, 1045, 1018, 862, 696, 509, and 503  $\text{cm}^{-1}$ ; HRMS (TOF)  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{13}\text{H}_7\text{Cl}_3\text{O}_2$ : 300.9584; found 300.9592.

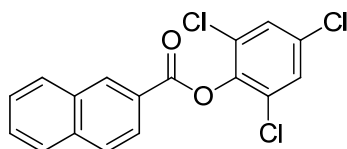


### 2,4,6-Trichlorophenyl 3,4-dihydronaphthalene-2-carboxylate (3b)

**3b** was obtained from **1f** and **2b** as a white crystal (m.p. 73  $^{\circ}\text{C}$ ) by method A. Yield: >99%.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.85 (s, 1H), 7.38 (s, 2H), 7.31-7.19 (m, 4H), 2.96 (t,  $J = 7.6$  Hz, 2H), 2.75 (t,  $J = 7.6$  Hz, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  163.5, 143.3, 139.9, 137.2, 132.0, 131.7, 130.3, 129.8,

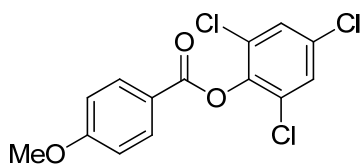
129.0, 128.5, 127.8, 126.9, 126.7, 27.4, and 22.2; IR (ATR) 1732, 1624, 1562, 1447, 1379, 1274, 1238, 1200, 1184, 1169, 1020, 957, 854, 756, 731, and 714  $\text{cm}^{-1}$ ; HRMS (TOF)  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{17}\text{H}_{11}\text{Cl}_3\text{O}_2$ : 352.9897; found 352.9887.



#### 2,4,6-Trichlorophenyl 2-naphthoate (**3c**)

**3c** was obtained from **1f** and **2c** as a white crystal (m.p. 115 °C) by method B. Yield: 90%.

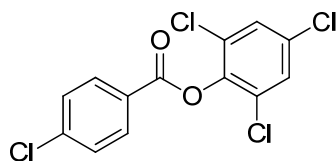
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.84 (s, 1H), 8.19 (dd,  $J$  = 8.8, 2.0, 1H), 7.97 (d,  $J$  = 7.6 Hz, 1H), 7.95 (d,  $J$  = 8.0 Hz, 1H), 7.89 (d,  $J$  = 8.0 Hz, 1H), 7.64-7.54 (m, 2H), 7.40 (s, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  163.1, 143.3, 136.1, 132.6, 132.4, 132.0, 130.5, 129.8, 129.5, 129.0, 128.6, 127.8, 127.0, 125.4, and 125.0; IR (ATR) 1746, 1562, 1447, 1277, 1219, 1184, 1124, 1040, 947, 908, 856, 818, 758, and 731  $\text{cm}^{-1}$ ; HRMS (TOF)  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{17}\text{H}_9\text{Cl}_3\text{O}_2$ : 350.9741; found 350.9742.



#### 2,4,6-Trichlorophenyl 4-methoxybenzoate (**3d**)

**3d** was obtained from **1f** and **2d** as a colorless oil by method A. Yield: 82%.

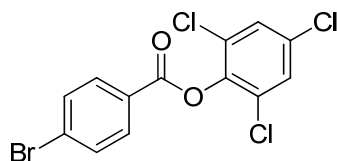
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.18 (d,  $J$  = 8.8 Hz, 2H), 7.40 (s, 2H), 7.00 (d,  $J$  = 8.8 Hz, 2H), 3.89 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  164.4, 162.6, 143.4, 132.7, 131.8, 129.9, 128.5, 120.0, 114.0, and 55.5; IR (ATR) 1744, 1605, 1510, 1449, 1258, 1227, 1167, 1138, 1043, 1024, 1003, 843, 818, 756, 689, and 610  $\text{cm}^{-1}$ ; HRMS (TOF)  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{14}\text{H}_9\text{Cl}_3\text{O}_3$ : 330.9690; found 330.9688.



#### 2,4,6-Trichlorophenyl 4-chlorobenzoate (**3e**)

**3e** was obtained from **1f** and **2e** as a colorless oil by method A. Yield: >99%.

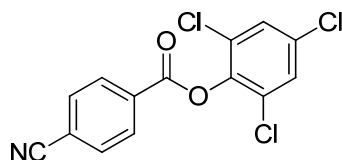
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.16 (d,  $J$  = 6.8 Hz, 2H), 7.50 (d,  $J$  = 6.8 Hz, 2H), 7.41 (s, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  162.1, 143.0, 140.9, 132.2, 131.8, 129.7, 129.1, 128.6, and 126.2; IR (ATR) 1746, 1591, 1566, 1447, 1402, 1387, 1256, 1223, 1175, 1142, 1090, 1076, 1011, 845, 820, and 746  $\text{cm}^{-1}$ ; HRMS (TOF)  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{13}\text{H}_6\text{Cl}_4\text{O}_2$ : 334.9195; found 334.9192.



**2,4,6-Trichlorophenyl 4-bromobenzoate (3f)**

**3f** was obtained from **1f** and **2f** as a white crystal (m.p. 74 °C) by method A. Yield: >99%.

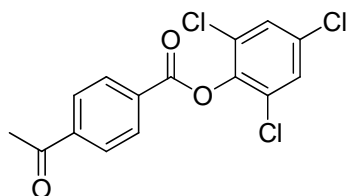
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.09 (dd,  $J = 8.0, 1.2$  Hz, 2H), 7.68 (dd,  $J = 8.0, 1.2$  Hz, 2H), 7.41 (d,  $J = 1.2$  Hz, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  162.3, 143.0, 132.23, 132.18, 132.0, 129.7, 128.7, and 126.7 (One aromatic carbon signal is missing.); IR (ATR) 1745, 1587, 1564, 1449, 1387, 1258, 1225, 1175, 1140, 1043, 1007, 820, and 743  $\text{cm}^{-1}$ ; HRMS (TOF)  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{13}\text{H}_6\text{BrCl}_3\text{O}_2$ : 378.8690; found 378.8683.



**2,4,6-Trichlorophenyl 4-cyanobenzoate (3g)**

**3g** was obtained from **1f** and **2g** as a white crystal (m.p. 106 °C) by method A. Yield: 94%.

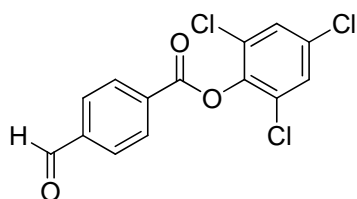
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.34 (d,  $J = 8.4$  Hz, 2H), 7.85 (d,  $J = 8.4$  Hz, 2H), 7.44 (s, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  161.4, 142.6, 138.4, 132.5, 131.6, 130.9, 129.5, 128.7, 117.65, and 117.57; IR (ATR) 2232, 1751, 1560, 1447, 1258, 1236, 1082, 1055, 1018, 854, 756, and 682  $\text{cm}^{-1}$ ; HRMS (TOF)  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{14}\text{H}_6\text{Cl}_3\text{NO}_2$ : 325.9537; found 325.9528.



**2,4,6-Trichlorophenyl 4-acetylbenzoate (3h)**

**3h** was obtained from **1f** and **2h** as a white crystal (m.p. 129 °C) by method A. Yield: >99%.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.32 (d,  $J = 8.0$  Hz, 2H), 8.10 (d,  $J = 8.0$  Hz, 2H), 7.43 (s, 2H), 2.68 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  197.3, 162.1, 142.9, 141.2, 132.3, 131.5, 130.8, 129.6, 128.7, 128.4, and 26.9; IR (ATR) 1746, 1686, 1566, 1450, 1389, 1229, 1082, 1051, 1011, 856, 758, and 689  $\text{cm}^{-1}$ ; HRMS (TOF)  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{15}\text{H}_9\text{Cl}_3\text{O}_3$ : 342.9690; found 342.9697.

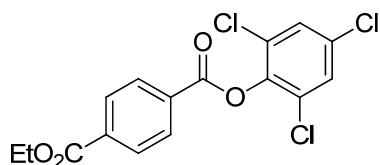




### 2,4,6-Trichlorophenyl 4-formylbenzoate (3i)

**3i** was obtained from **1f** and **2i** as a white crystal (m.p. 93 °C) by method A. Yield: 99%.

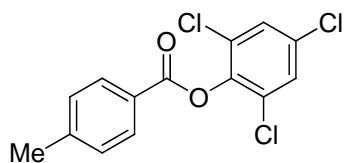
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.20 (s, 1H), 8.40 (d,  $J$  = 8.0 Hz, 2H), 8.05 (d,  $J$  = 8.0 Hz, 2H), 7.43 (s, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  191.3, 162.0, 142.8, 140.0, 132.6, 132.4, 131.1, 129.7, 128.7 and 128.0; IR (ATR) 1757, 1705, 1564, 1449, 1387, 1227, 1200, 1140, 1045, 1013, 854, 820, and 746  $\text{cm}^{-1}$ ; HRMS (TOF)  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{14}\text{H}_7\text{Cl}_3\text{O}_3$ : 328.9534; found 328.9536.



### 2,4,6-Trichlorophenyl 4-ethoxycarbonylbenzoate (3j)

**3j** was obtained from **1f** and **2j** as a white crystal (m.p. 99 °C) by method A. Yield: 85%.

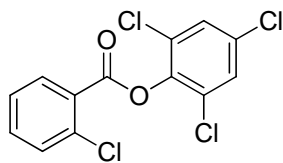
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.30 (d,  $J$  = 8.4 Hz, 2H), 8.20 (d,  $J$  = 8.4 Hz, 2H), 7.43 (s, 2H), 4.44 (q,  $J$  = 6.8 Hz, 2H), 1.43 (t,  $J$  = 6.8 Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  165.4, 162.2, 143.0, 135.5, 132.3, 131.4, 130.4, 129.8, 129.7, 128.7, 61.6, and 14.2; IR (ATR) 1746, 1717, 1566, 1447, 1267, 1254, 1229, 1105, 1045, 1012, 849, 880, and 725  $\text{cm}^{-1}$ ; HRMS (TOF)  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{16}\text{H}_{11}\text{Cl}_3\text{O}_4$ : 372.9796; found 372.9800.



### 2,4,6-Trichlorophenyl 4-methylbenzoate (3k)

**3k** was obtained from **1f** and **2k** as a white crystal (m.p. 68 °C) by method B. Yield: 81%.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.12 (d,  $J$  = 8.4 Hz, 2H), 7.41 (s, 2H), 7.33 (d,  $J$  = 8.4 Hz, 2H), 2.46 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  162.9, 145.3, 143.3, 131.9, 130.6, 129.9, 129.5, 128.6, 125.1, and 21.8; IR (ATR) 1742, 1611, 1564, 1447, 1387, 1260, 1225, 1179, 1042, 1015, 854, 818, and 741  $\text{cm}^{-1}$ ; HRMS (TOF)  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{14}\text{H}_9\text{Cl}_3\text{O}_2$ : 314.9741; found 314.9746.

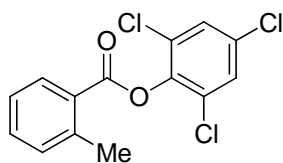


### 2,4,6-Trichlorophenyl 2-chlorobenzoate (3m)

**3m** was obtained from **1f** and **2m** as a white crystal (m.p. 57 °C) by method A. Reaction temperature was 45 °C. Yield: 96%.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.18 (d,  $J$  = 8.0 Hz, 1H), 7.55-7.52 (m, 2H), 7.43 (s, 2H), 7.42-7.39 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  161.2, 142.8, 135.1, 133.8, 132.3, 132.2, 131.5, 129.7, 128.6, 127.5,

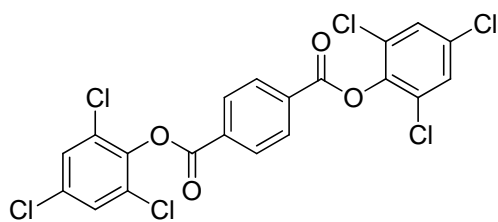
and 126.8; IR (ATR) 1753, 1589, 1564, 1445, 1387, 1219, 1130, 1086, 1016, 856, 820, and 740  $\text{cm}^{-1}$ ; HRMS (TOF)  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{13}\text{H}_6\text{Cl}_4\text{O}_2$ : 334.9195; found 334.9196.



**2,4,6-Trichlorophenyl 2-methylbenzoate (3n)**

**3n** was obtained from **1f** and **2n** as a colorless oil by method A. Reaction temperature was 45 °C. Yield: 82%.

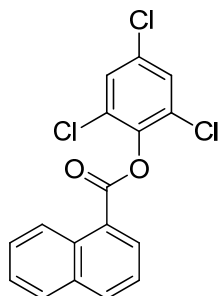
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.23 (d,  $J = 7.2$  Hz, 1H), 7.52-7.49 (m, 1H), 7.42 (s, 2H), 7.40-7.36 (m, 2H), 2.67 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  163.3, 143.3, 141.8, 133.3, 132.0, 131.9, 131.5, 129.9, 128.6, 127.1, 126.0, and 21.7; IR (ATR) 1751, 1562, 1447, 1385, 1287, 1244, 1219, 1130, 1011, 858, 818, 804, 791, and 731  $\text{cm}^{-1}$ ; HRMS (TOF)  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{14}\text{H}_9\text{Cl}_3\text{O}_2$ : 314.9741; found 314.9748.



**Bis(2,4,6-trichlorophenyl) terephthalate (3o)**

**3o** was obtained from **1f** and **2o** or **2oa** as a white crystal (m.p. 179 °C). Yield: 75% from **2o** by method A (2.5 equiv of **1f** and 4 equiv of  $\text{NBu}_3$  were used in the presence of 5 mol % of  $\text{Pd}(\text{OAc})_2$  and 10 mol % of xantphos). Yield: 92% from **2oa** by method B (3 equiv of **1f** and 3 equiv of  $\text{NEt}_3$  were used in the presence of 5 mol % of  $\text{Pd}(\text{OAc})_2$  and 10 mol % of xantphos).

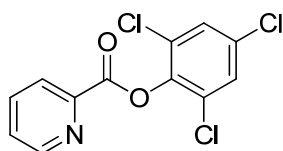
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.40 (s, 4H), 7.45 (s, 4H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  161.9, 142.9, 132.8, 132.4, 130.8, 129.6, and 128.7; IR (ATR) 1751, 1562, 1447, 1254, 1227, 1136, 1049, 1011, 853, 820 and 708  $\text{cm}^{-1}$ ; HRMS (TOF)  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{20}\text{H}_8\text{Cl}_6\text{O}_4$ : 522.8627; found 522.8636.



**2,4,6-Trichlorophenyl 1-naphthoate (3p)**

**3p** was obtained from **1f** and **2p** as a white crystal (m.p. 94 °C) by method A. Reaction temperature was 45 °C. Yield: 99%.

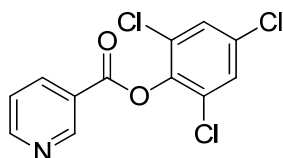
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.98 (d,  $J$  = 9.2 Hz, 1H), 8.56 (dd,  $J$  = 7.6, 1.2 Hz, 1H), 8.11 (d,  $J$  = 8.4 Hz, 1H), 7.90 (d,  $J$  = 8.4 Hz, 1H), 7.65 (ddd,  $J$  = 7.6, 6.8, 1.6 Hz, 1H), 7.59-7.53 (m, 2H), 7.43 (s, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  163.2, 143.2, 134.9, 133.8, 132.0, 131.8, 131.7, 129.9, 128.7, 128.6, 128.5, 126.6, 125.5, 124.5, and 124.2; IR (ATR) 3071, 1740, 1560, 1447, 1229, 1182, 1099, 1072, 966, 862, 804, and  $768\text{ cm}^{-1}$ ; HRMS (TOF)  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{17}\text{H}_9\text{Cl}_3\text{O}_2$ : 350.9741; found 350.9741.



#### 2,4,6-Trichlorophenyl picolinate (3q)

**3q** was obtained from **1f** and **2q** or **2qa** as a white crystal (m.p.  $121\text{ }^\circ\text{C}$ ). Yield: 88% from **2qa** by method A. Yield: >99% from **2q** by method A (The reaction temperature was  $45\text{ }^\circ\text{C}$ ).

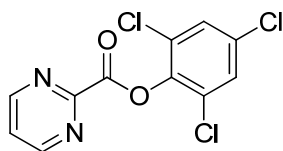
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.90-8.87 (m, 1H), 8.32 (d,  $J$  = 8.0 Hz, 1H), 7.95 (td,  $J$  = 8.0, 1.6 Hz, 1H), 7.61 (ddd,  $J$  = 7.2, 4.4, 1.6 Hz, 1H), 7.43 (s, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  161.4, 150.4, 145.9, 143.1, 137.2, 132.2, 129.5, 128.6, 127.9, and 126.2; IR (ATR) 1746, 1564, 1450, 1437, 1288, 1233, 1080, 1067, 1043, 739, and  $694\text{ cm}^{-1}$ ; HRMS (TOF)  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{12}\text{H}_6\text{Cl}_3\text{NO}_2$ : 301.9537; found 301.9545.



#### 2,4,6-Trichlorophenyl nicotinate (3r)

**3r** was obtained from **1f** and **2r** as a white crystal (m.p.  $47\text{ }^\circ\text{C}$ ) by method B. Yield: 86%.

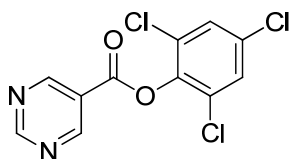
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.44 (d,  $J$  = 2.0 Hz, 1H), 8.91 (dd,  $J$  = 4.8, 1.2 Hz, 1H), 8.48 (ddd,  $J$  = 8.4, 2.0, 1.2 Hz, 1H), 7.50 (dd,  $J$  = 8.4, 4.8 Hz, 1H), 7.44 (s, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  161.7, 154.6, 151.6, 142.7, 137.8, 132.4, 129.6, 128.7, 124.1, and 123.6; IR (ATR) 1751, 1587, 1562, 1450, 1420, 1267, 1229, 1061, 1016, 862, 725, and  $696\text{ cm}^{-1}$ ; HRMS (TOF)  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{12}\text{H}_6\text{Cl}_3\text{NO}_2$ : 301.9537; found 301.9543.



#### 2,4,6-Trichlorophenyl pyrimidine-2-carboxylate (3s)

**3s** was obtained from **1f** and **2s** as a colorless oil by method A. Yield: 74%.

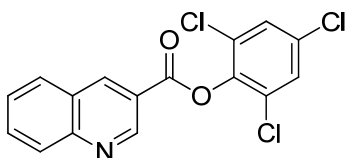
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.07 (d,  $J$  = 4.8 Hz, 2H), 7.62 (d,  $J$  = 4.8 Hz, 1H), 7.45 (s, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  159.4, 158.2, 155.0, 142.9, 132.6, 129.4, 128.8, 128.0, and 123.9; IR (ATR) 1771, 1562, 1447, 1304, 1234, 1109, 1090, 1063, 856, 820, 766, 752, 685, and  $629\text{ cm}^{-1}$ ; HRMS (TOF)  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{11}\text{H}_5\text{Cl}_3\text{N}_2\text{O}_2$ : 302.9489; found 302.9483.



#### 2,4,6-Trichlorophenyl pyrimidine-5-carboxylate (**3t**)

**3t** was obtained from **1f** and **2t** as a white crystal (m.p. 75 °C) by method B. Yield: 74%.

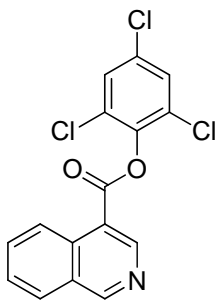
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.51 (s, 2H), 9.50 (s, 1H), 7.46 (s, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  162.3, 160.1, 158.6, 142.2, 132.8, 129.5, 128.8, and 122.5; IR (ATR) 1761, 1584, 1562, 1450, 1435, 1269, 1233, 1121, 1062, 1020, 862, 818, and 710  $\text{cm}^{-1}$ ; HRMS (TOF)  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{11}\text{H}_5\text{Cl}_3\text{N}_2\text{O}_2$ : 302.9489; found 302.9481.



#### 2,4,6-Trichlorophenyl quinoline-3-carboxylate (**3u**)

**3u** was obtained from **1f** and **2u** as a white crystal (m.p. 143 °C) by method B. Yield: 90%.

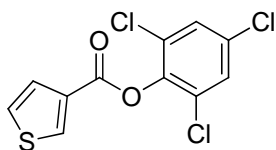
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.61 (d,  $J$  = 2.4 Hz, 1H), 9.07 (d,  $J$  = 2.0 Hz, 1H), 8.22 (d,  $J$  = 8.8 Hz, 1H), 7.98 (d,  $J$  = 8.4 Hz, 1H), 7.90 (ddd,  $J$  = 8.8, 8.0, 1.2 Hz, 1H), 7.67 (ddd,  $J$  = 8.4, 8.0, 1.2 Hz, 1H), 7.43 (s, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  161.8, 150.3, 149.9, 142.8, 140.1, 132.6, 132.4, 129.7, 129.6, 129.3, 128.7, 127.8, 126.6, and 120.8; IR (ATR) 1749, 1618, 1562, 1449, 1287, 1221, 1123, 966, 860, 789, and 760  $\text{cm}^{-1}$ ; HRMS (TOF)  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{16}\text{H}_8\text{Cl}_3\text{NO}_2$ : 351.9693; found 351.9702.



#### 2,4,6-Trichlorophenyl isoquinoline-4-carboxylate (**3v**)

**3v** was obtained from **1f** and **2v** as a white crystal (m.p. 156 °C) by method B. Yield: 76%.

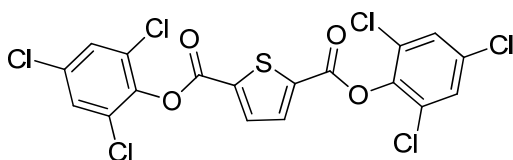
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.54 (s, 1H), 9.48 (s, 1H), 8.96 (d,  $J$  = 8.8 Hz, 1H), 8.09 (d,  $J$  = 8.4 Hz, 1H), 7.89 (dd,  $J$  = 8.4, 7.6 Hz, 1H), 7.73 (dd,  $J$  = 8.8, 7.6 Hz, 1H), 7.46 (s, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  162.5, 158.2, 148.0, 142.9, 134.0, 132.9, 132.3, 129.8, 128.7, 128.5, 128.1, 124.7, and 118.3 (One aromatic carbon signal is missing.); IR (ATR) 1744, 1562, 1375, 1225, 1213, 1157, 1121, 1096, 980, 957, 856, 770, and 748  $\text{cm}^{-1}$ ; HRMS (TOF)  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{16}\text{H}_8\text{Cl}_3\text{NO}_2$ : 351.9693; found 351.9702.



#### 2,4,6-Trichlorophenyl thiophene-3-carboxylate (**3w**)

**3w** was obtained from **1f** and **2w** or **2wa** as a white crystal (m.p. 44 °C). Yield: 98% from **2w** by method A. Yield: 84% from **2wa** by method B.

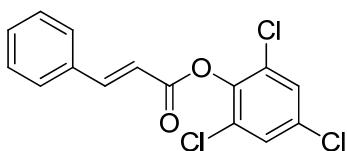
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.40 (dd,  $J = 2.8, 1.2$  Hz, 1H), 7.69 (dd,  $J = 4.8, 1.2$  Hz, 1H), 7.40 (s, 2H), 7.39 (dd,  $J = 4.8, 2.8$  Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  158.5, 142.9, 135.2, 132.0, 130.9, 129.8, 128.6, 128.2, and 126.7; IR (ATR) 1746, 1562, 1449, 1396, 1387, 1229, 1177, 1045, 854, 816, 802, and 733  $\text{cm}^{-1}$ ; HRMS (TOF)  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{11}\text{H}_5\text{Cl}_3\text{O}_2\text{S}$ : 306.9149; found 306.9149.



#### Bis(2,4,6-trichlorophenyl) thiophene-2,5-dicarboxylate (**3x**)

**3x** was obtained from **1f** and **2x** as a white crystal (m.p. 205 °C) by method A (3 equiv of **1f** and 3 equiv of  $\text{NEt}_3$  were used in the presence of 5 mol % of  $\text{Pd}(\text{OAc})_2$  and 10 mol % of xantphos). Yield: 76%.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.07 (s, 2H), 7.44 (s, 4H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  157.4, 142.4, 137.5, 135.4, 132.7, 129.7, and 128.7; IR (ATR) 1753, 1740, 1566, 1449, 1260, 1217, 1126, 1015, 997, 843, 818, 733, and 719  $\text{cm}^{-1}$ ; HRMS (TOF)  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{18}\text{H}_6\text{Cl}_6\text{O}_4\text{S}$ : 528.8191; found 528.8200.



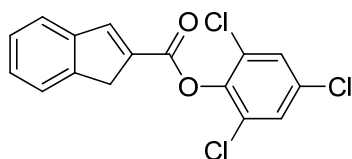
#### 2,4,6-Trichlorophenyl cinnamate (**3y**)

**3y** ( $E/Z = 97/3$ ) was obtained from **1f** and **2y** ( $E/Z = 87/13$ ) as a colorless oil by method A. Yield: 88%.

*E*-form:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.94 (d,  $J = 16.0$  Hz, 1H), 7.60-7.56 (m, 2H), 7.46-7.32 (m, 3H), 7.36 (s, 2H), 6.66 (d,  $J = 16.0$  Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  162.9, 148.3, 143.1, 133.7, 131.8, 131.1, 129.7, 129.0, 128.50, 128.45, 115.2.

*Z*-form:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  *inter alia* 7.73-7.70 (m, 2H), 6.24 (d,  $J = 12.8$  Hz, 1H).

*E/Z*-mixture: IR (ATR) 1740, 1632, 1445, 1217, 1194, 1103, 957, 854, 758, 731, and 702  $\text{cm}^{-1}$ ; HRMS (TOF)  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{15}\text{H}_9\text{Cl}_3\text{O}_2$ : 326.9741; found 326.9739.



### 2,4,6-Trichlorophenyl 1H-indene-2-carboxylate (**3z**)

**3z** was obtained from **1f** and **2z** as a white crystal (m.p. 121 °C) by method A. Yield: 97%.

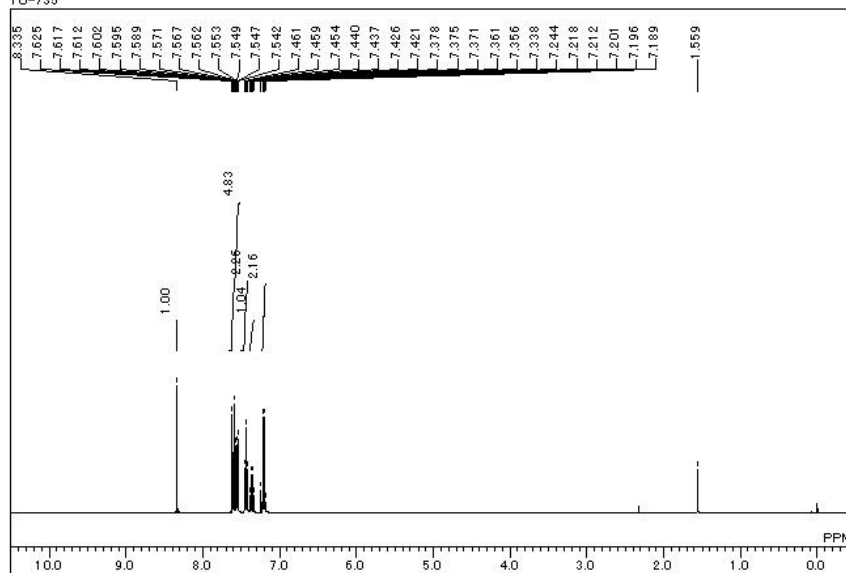
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.06 (s, 1H), 7.59 (dd,  $J = 6.4, 2.0$  Hz, 1H), 7.55 (d,  $J = 7.2$  Hz, 1H), 7.42-7.33 (m, 2H), 7.39 (s, 2H), 3.85 (d,  $J = 1.6$  Hz, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  160.7, 145.2, 144.8, 143.1, 142.2, 134.2, 131.8, 129.9, 128.54, 128.47, 127.1, 124.4, 124.0, and 38.4; IR (ATR) 1724, 1560, 1447, 1387, 1335, 1229, 1173, 1130, 1011, 850, 756, and 714  $\text{cm}^{-1}$ ; HRMS (TOF)  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{16}\text{H}_9\text{Cl}_3\text{O}_2$ : 338.9741; found 338.9751.

## 10. References

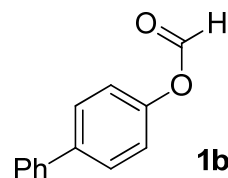
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## 11. NMR spectra of obtained compounds (1b-g, 2b, 2z, 3a-z, 8-17)

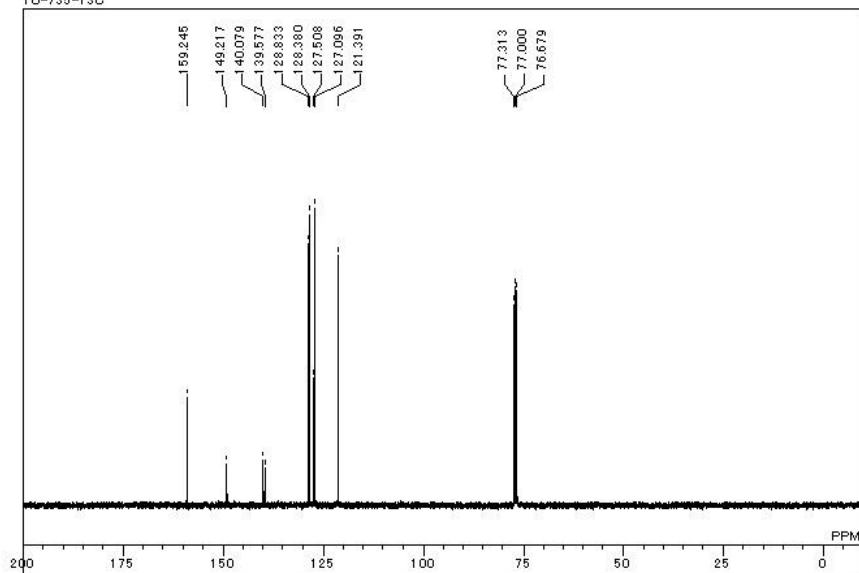
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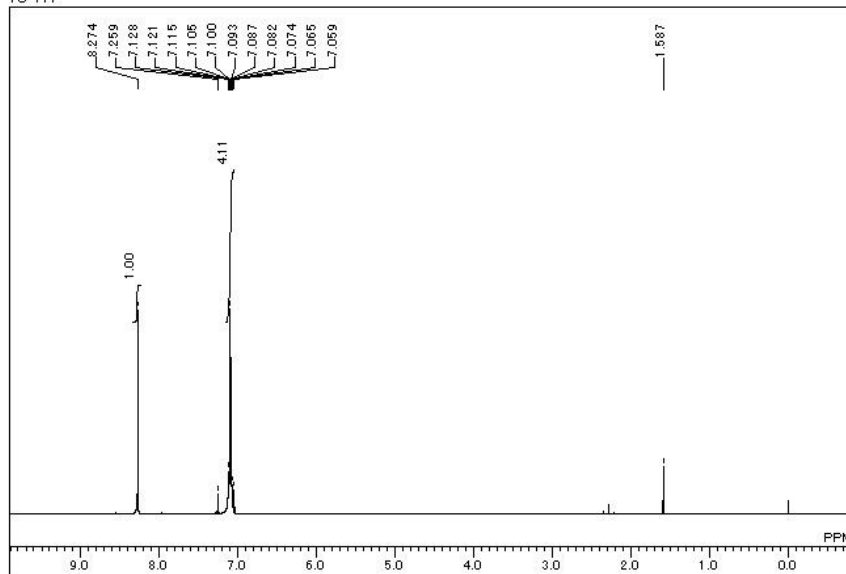


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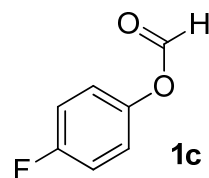
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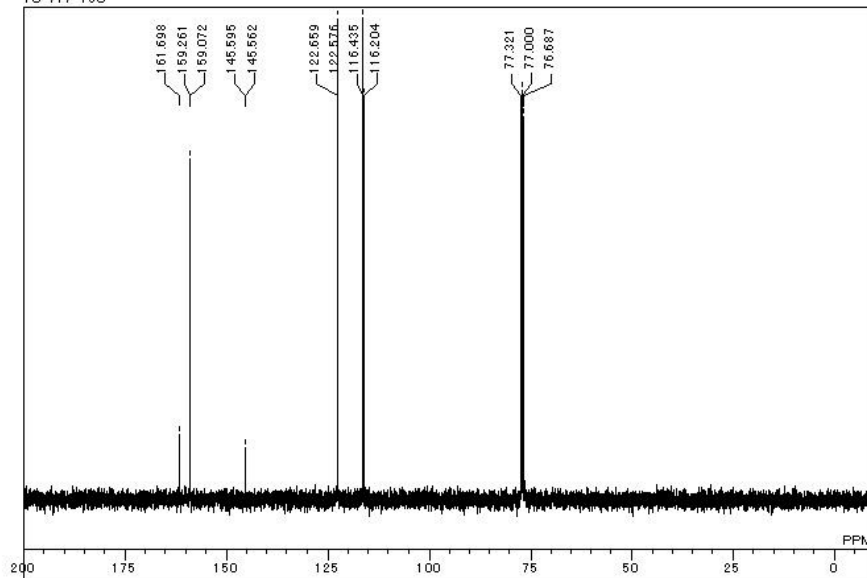


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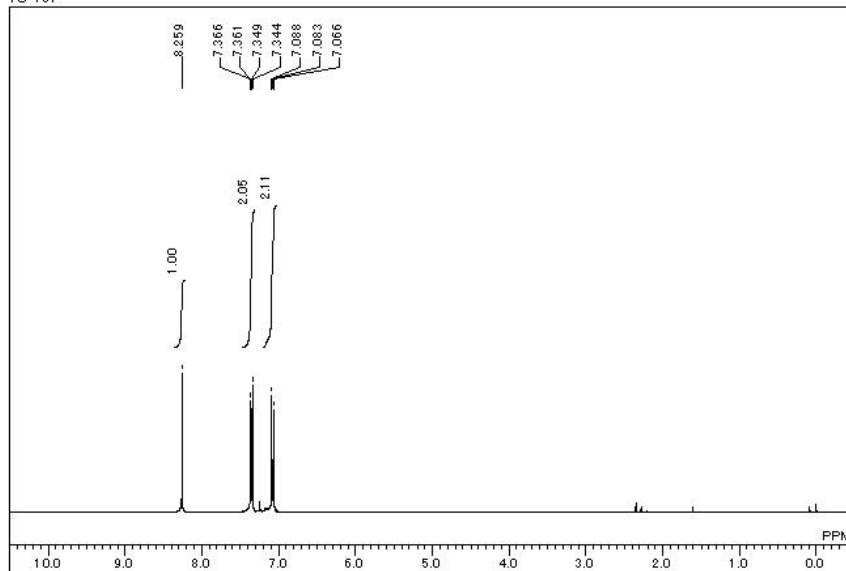


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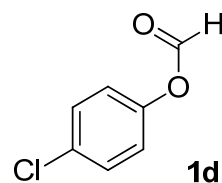
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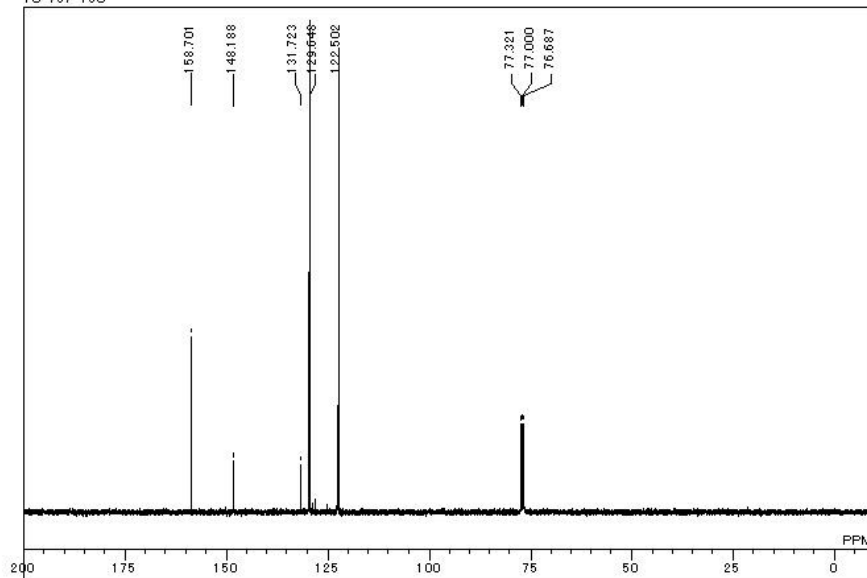
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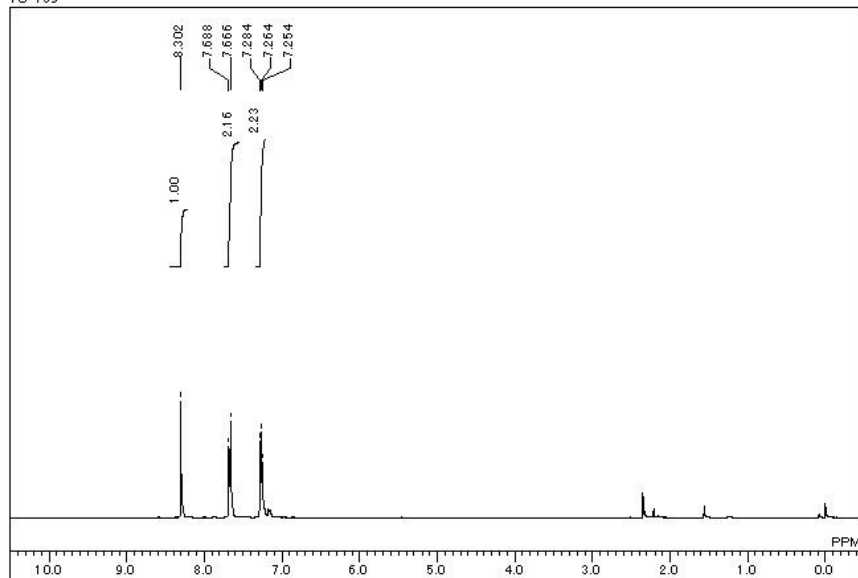


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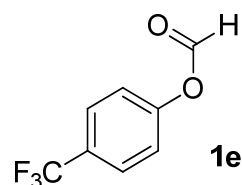


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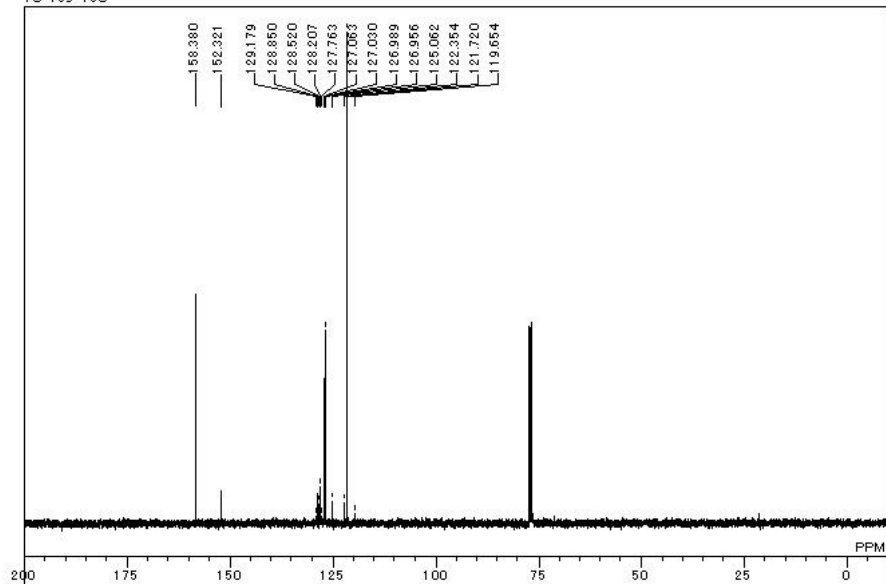
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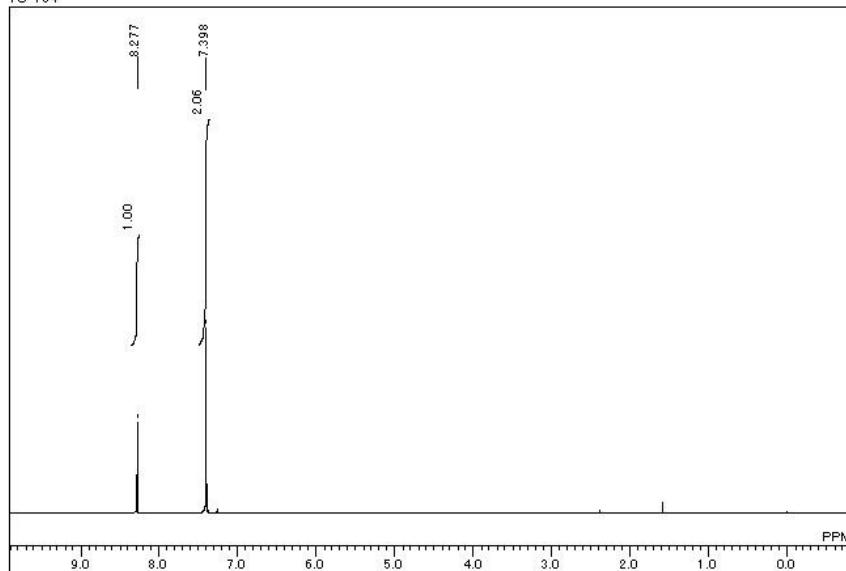


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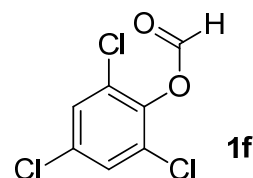


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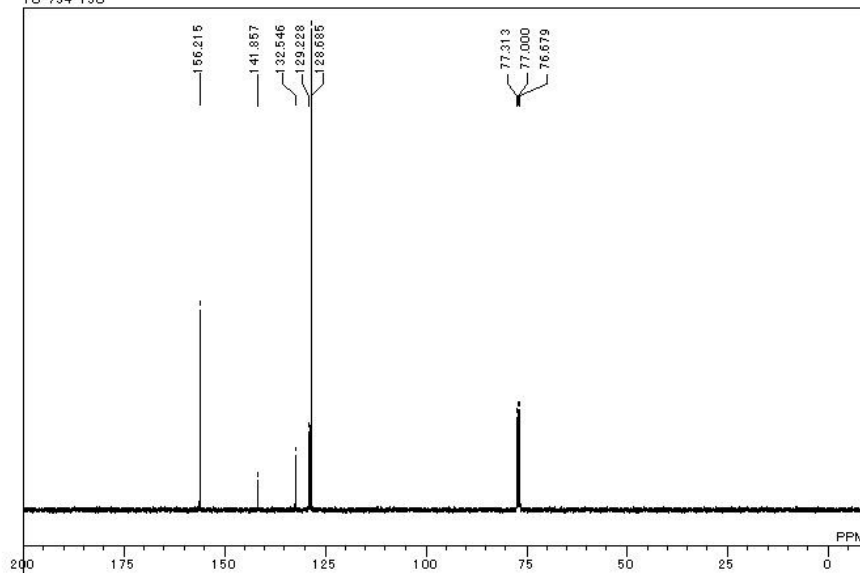
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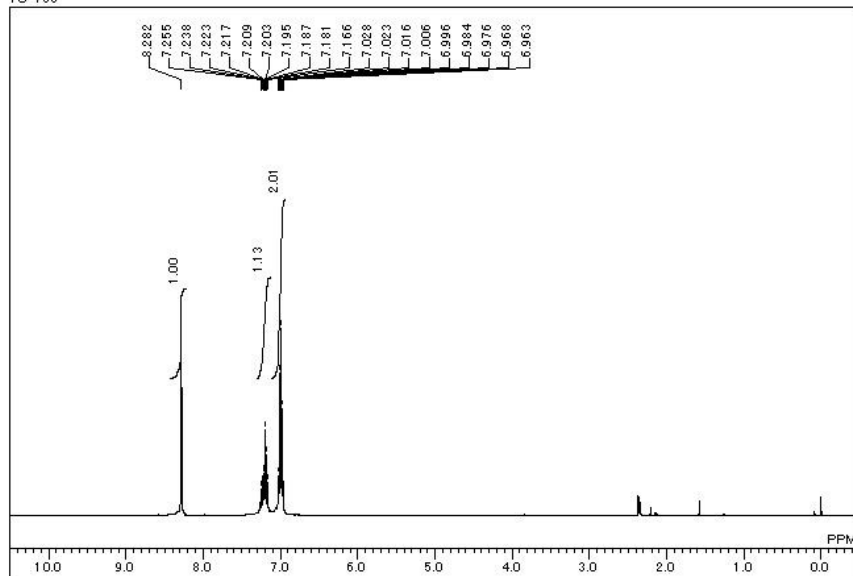


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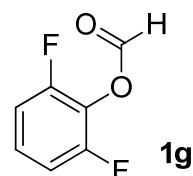


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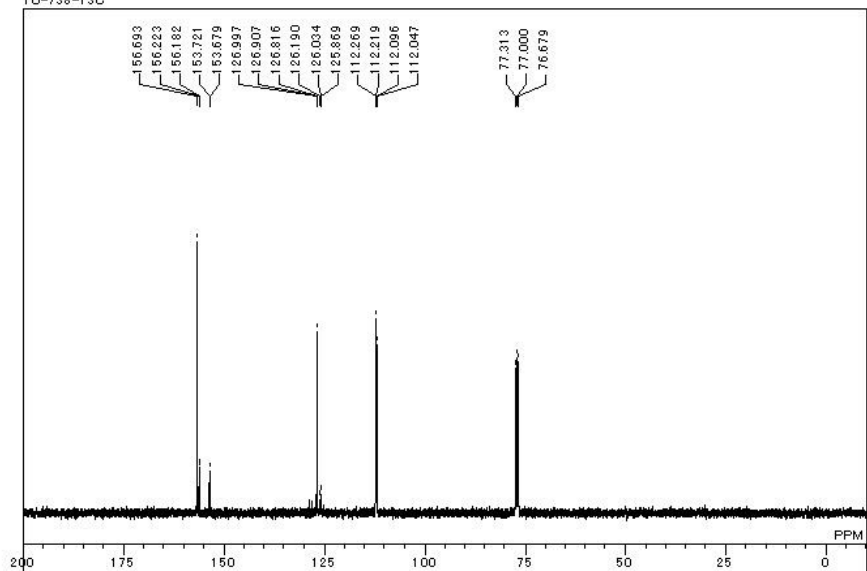
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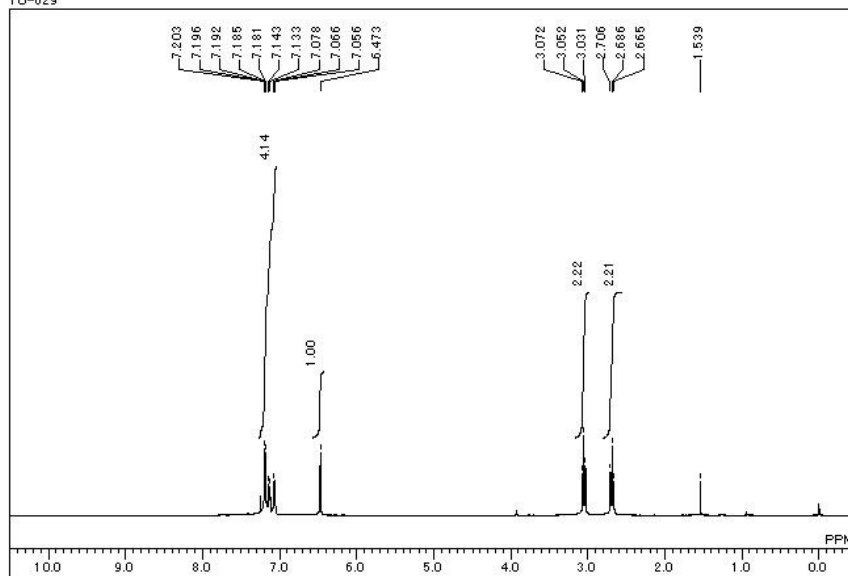


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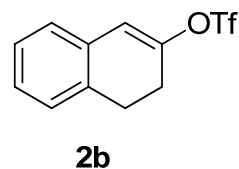
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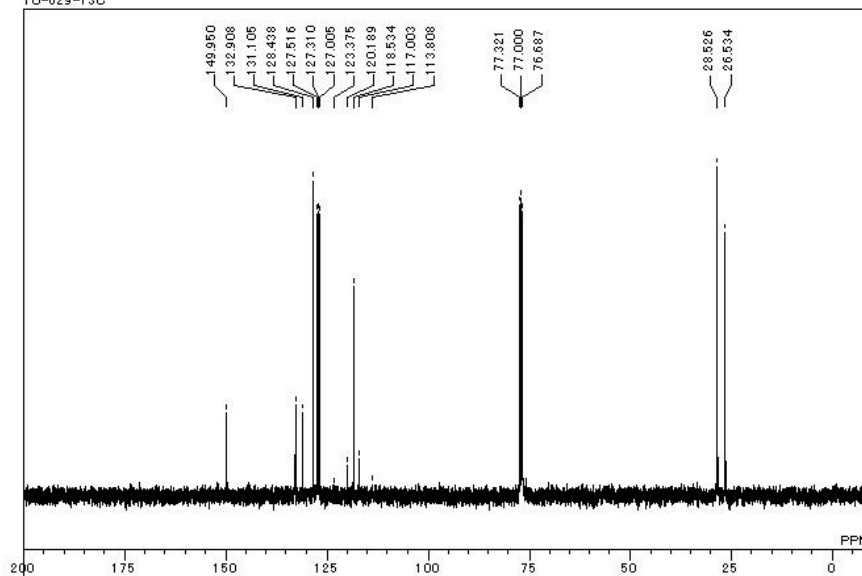


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FREQU  
SCANS  
AQTM  
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IRNUC  
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BF  
RGAIN

F:\JACS-Carboxylation NMR\TU-629  
TU-629  
Wed May 23 23:29:11 2012  
1H  
NON  
399.65 MHz  
124.00 KHz  
10500.00 Hz  
16384  
7992.01 Hz  
8  
2.0500 sec  
4.9500 sec  
6.20 usec  
1H  
24.7 c  
ODCL3  
0.00 ppm  
0.12 Hz  
13



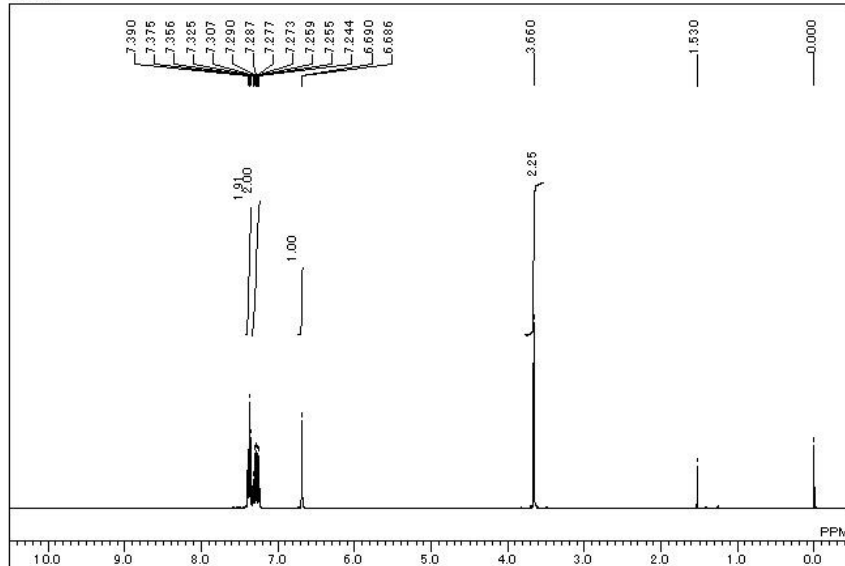
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TU-629-13C



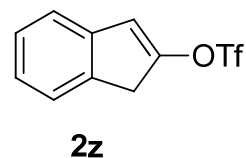
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AQTM  
PD  
PWI  
IRNUC  
CTEMP  
SLVNT  
EXREF  
BF  
RGAIN

F:\JACS-Carboxylation NMR\TU-629-13C  
TU-629-13C  
Wed May 23 23:39:57 2012  
13C  
BCM  
100.40 MHz  
125.00 KHz  
10500.00 Hz  
32768  
27118.64 Hz  
128  
1.2083 sec  
1.7920 sec  
5.50 usec  
1H  
25.1 c  
ODCL3  
77.00 ppm  
1.20 Hz  
27

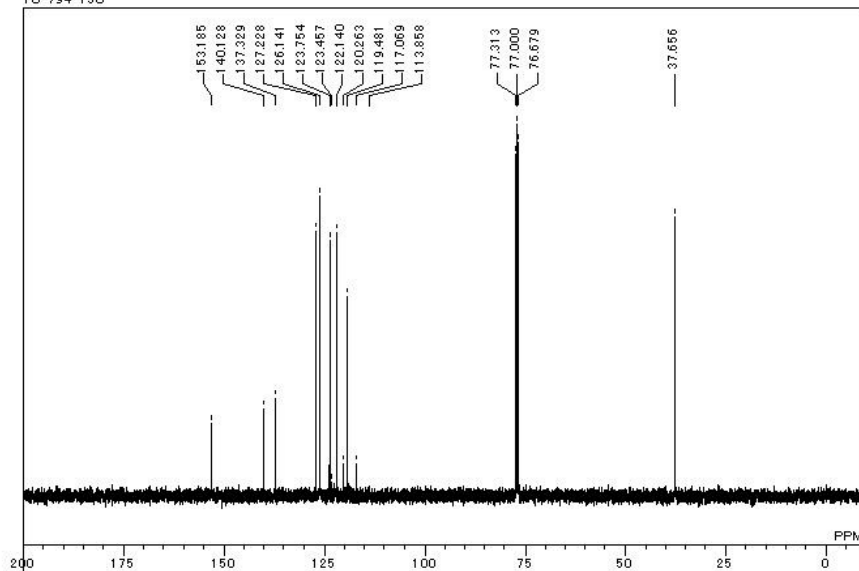
F:\JACS-Carbonylation NMR\TU-7941NON.E10.FT.als  
TU-794



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COMNT TU-794  
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GBNUC 1H  
EXMOD NON  
OBFRO 399.65 MHz  
OBSET 124.00 KHz  
OBFIN 10500.00 Hz  
POINT 16384  
FREQU 7992.01 Hz  
SCANS 8  
AQTM 2.0500 sec  
PD 4.9500 sec  
PWI 6.20 usec  
IRNUC 1H  
CTEMP 24.1 c  
SLVNT CDCL3  
EXREF 0.00 ppm  
BF 0.12 Hz  
RGAIN 14

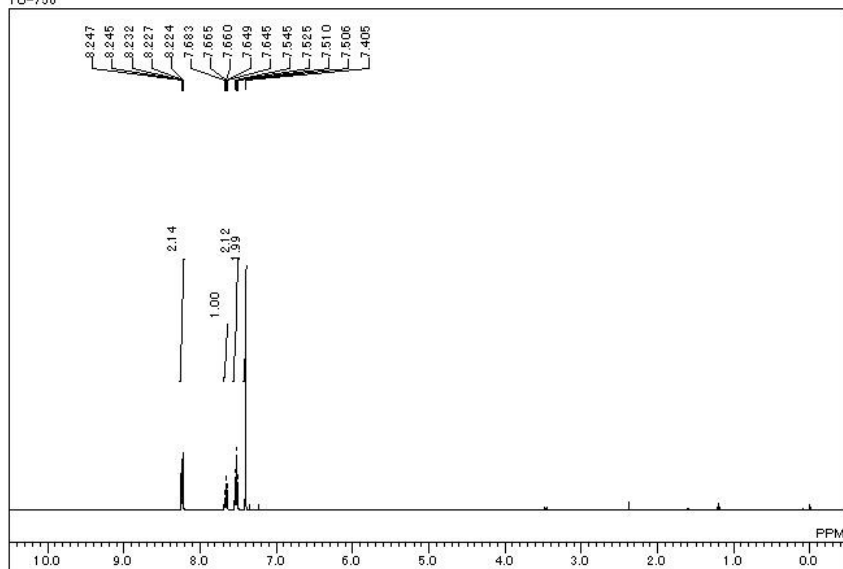


F:\JACS-Carbonylation NMR\TU-794-13C1BCM.E17.FT.als  
TU-794-13C

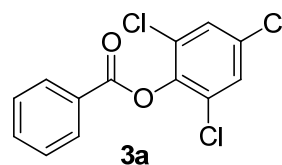


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OBSET 125.00 KHz  
OBFIN 10500.00 Hz  
POINT 32768  
FREQU 27118.64 Hz  
SCANS 128  
AQTM 1.2083 sec  
PD 1.7920 sec  
PWI 5.50 usec  
IRNUC 1H  
CTEMP 24.5 c  
SLVNT CDCL3  
EXREF 77.00 ppm  
BF 1.20 Hz  
RGAIN 26

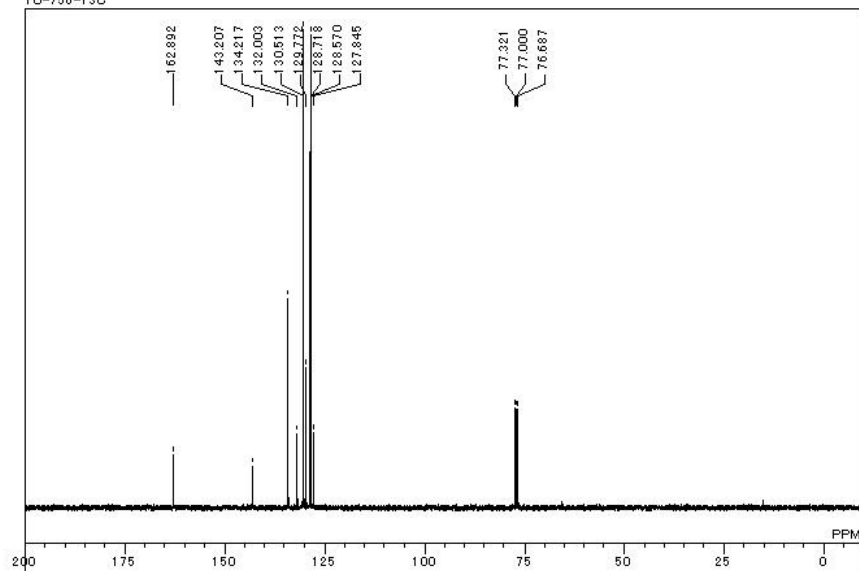
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TU-756



DFILE F:\JACS-Carbonylation NMR\TU-  
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OBNUC 1H  
EXMOD NON  
OBFRQ 399.65 MHz  
OBSET 124.00 KHz  
OBFIN 10500.00 Hz  
POINT 16384  
FREQU 7992.01 Hz  
SCANS 8  
AQTM 2.0500 sec  
PD 4.9500 sec  
PW 6.20 usec  
IRNUC 1H  
CTEMP 23.1 c  
SLVNT CDCL3  
EXREF 0.00 ppm  
BF 0.12 Hz  
RGAIN 10

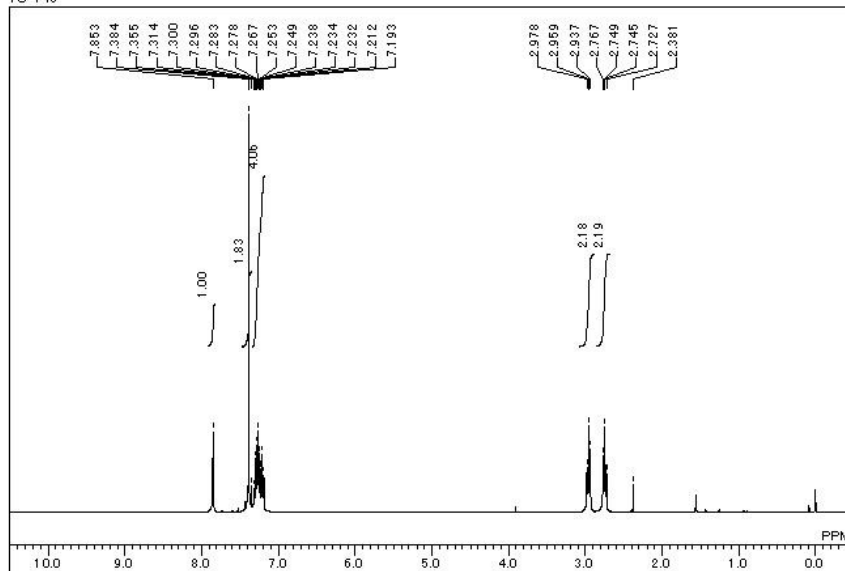


F:\JACS-Carbonylation NMR\TU-756-1301BCM.E4.FT.als  
TU-756-130

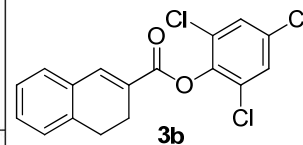


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OBSET 125.00 KHz  
OBFIN 10500.00 Hz  
POINT 32768  
FREQU 27113.64 Hz  
SCANS 128  
AQTM 1.2083 sec  
PD 1.7920 sec  
PW 6.50 usec  
IRNUC 1H  
CTEMP 24.0 c  
SLVNT CDCL3  
EXREF 77.00 ppm  
BF 1.20 Hz  
RGAIN 26

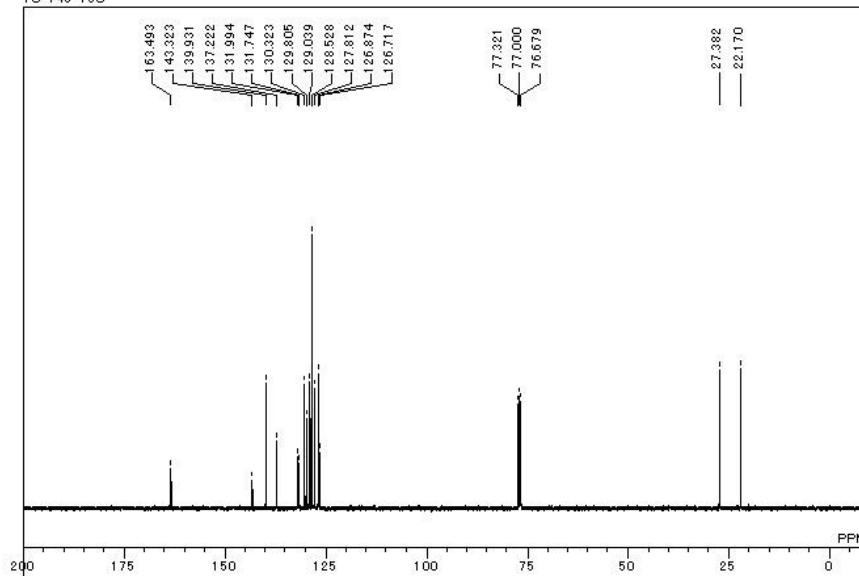
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TU-743



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COMINT TU-743  
DATIM Fri Jun 15 11:02:11 2012  
OBNUC 1H  
EXMOD NON  
OBFRO 399.65 MHz  
OBSET 124.00 KHz  
OBFIN 10500.00 Hz  
POINT 16384  
FREQU 7992.01 Hz  
SCANS 8  
AQGTM 2.0500 sec  
PD 4.9500 sec  
PWI 6.20 usec  
IRNUC 1H  
CTEMP 23.1 c  
SLVNT CDCL3  
EXREF 0.00 ppm  
BF 0.12 Hz  
RGAIN 11



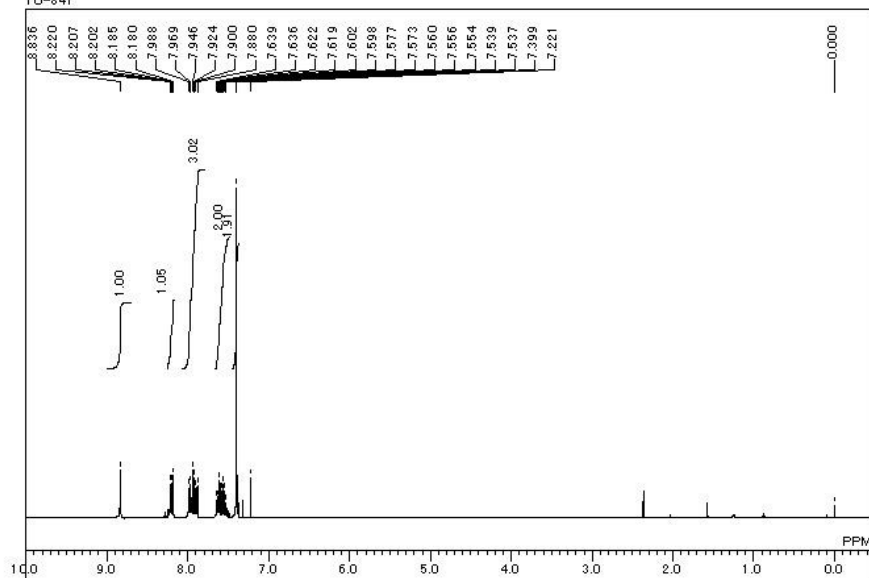
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TU-743-13C



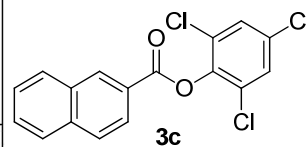
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OBNUC 13C  
EXMOD BOM  
OBFRO 100.40 MHz  
OBSET 125.00 KHz  
OBFIN 10500.00 Hz  
POINT 32768  
FREQU 27118.64 Hz  
SCANS 256  
AQGTM 1.2083 sec  
PD 1.7920 sec  
PWI 5.50 usec  
IRNUC 1H  
CTEMP 23.0 c  
SLVNT CDCL3  
EXREF 77.00 ppm  
BF 1.20 Hz  
RGAIN 26



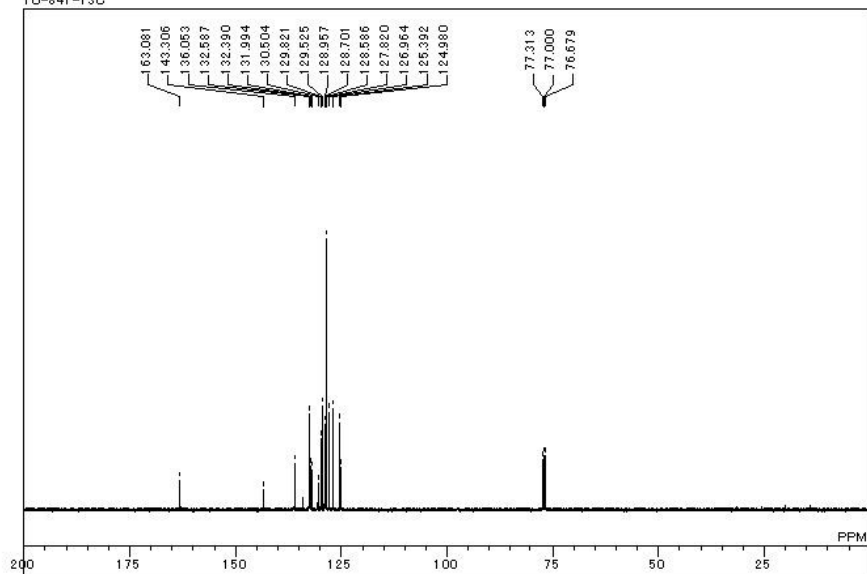
F:\JACS-Carbonylation NMR\TU-84111NON.E1\_FT.als  
TU-841



DFILE F:\JACS-Carbonylation NMR\TU-  
COMNT TU-841  
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OBNUC 1H  
EXMOD NDN  
OBFRQ 399.65 MHz  
OBSET 124.00 KHz  
OBFIN 10500.00 Hz  
POINT 16384  
FREQU 7992.01 Hz  
SCANS 8  
AQTM 2.0500 sec  
PD 4.9500 sec  
PWI 6.20 usec  
IRNUC 1H  
CTEMP 26.3 c  
SLVNT CDCL3  
EXREF 0.00 ppm  
BF 0.12 Hz  
RGAIN 10

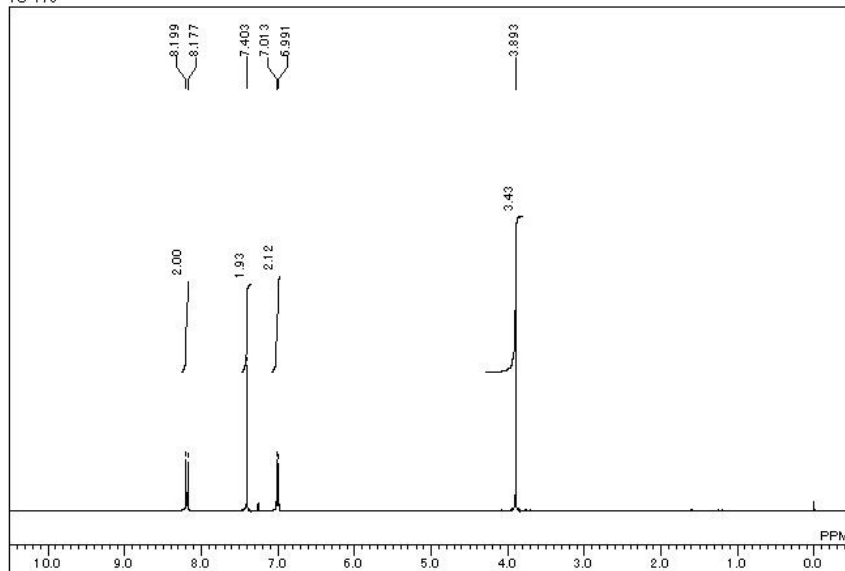


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TU-841-13C

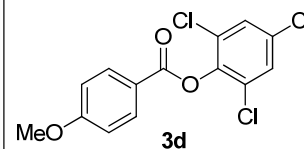


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EXMOD BCM  
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OBSET 125.00 KHz  
OBFIN 10500.00 Hz  
POINT 32768  
FREQU 27118.64 Hz  
SCANS 128  
AQTM 1.2083 sec  
PD 1.7920 sec  
PWI 5.50 usec  
IRNUC 1H  
CTEMP 26.3 c  
SLVNT CDCL3  
EXREF 77.00 ppm  
BF 1.20 Hz  
RGAIN 26

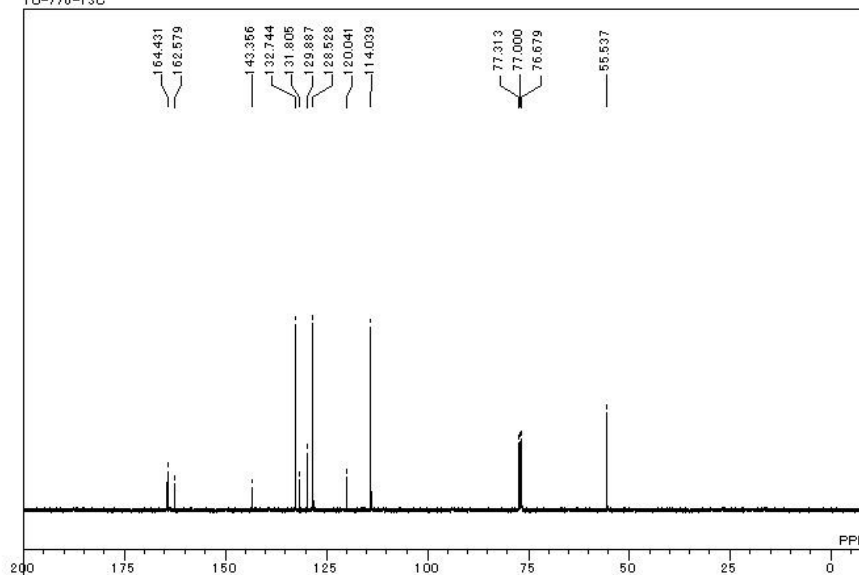
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TU-776



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OBNJC 1H  
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OBFRO 399.65 MHz  
OBSET 124.00 KHz  
OBFIN 10500.00 Hz  
POINT 16384  
FREQU 7992.01 Hz  
SCANS 8  
AQTM 2.0500 sec  
PD 4.9500 sec  
PWI 6.20 usec  
IRNJC 1H  
CTEMP 24.1 c  
SLVNT CDCL3  
EXREF 0.00 ppm  
BF 0.12 Hz  
RGAIN 13

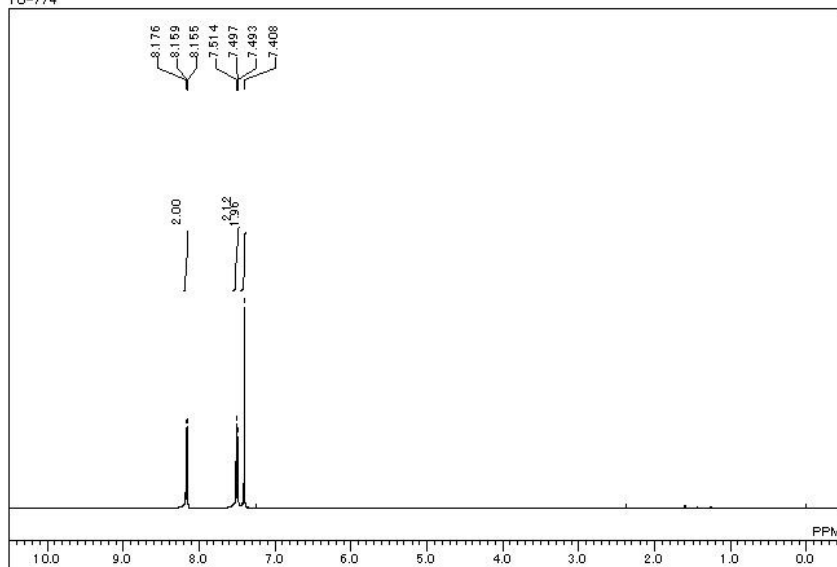


F:\JACS-Carbonylation NMR\TU-776-13C1BOM\_E33\_FT.als  
TU-776-13C

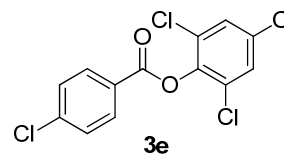


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EXMOD BOM  
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OBSET 125.00 KHz  
OBFIN 10500.00 Hz  
POINT 32768  
FREQU 27118.64 Hz  
SCANS 128  
AQTM 1.2083 sec  
PD 1.7920 sec  
PWI 5.50 usec  
IRNJC 1H  
CTEMP 24.7 c  
SLVNT CDCL3  
EXREF 77.00 ppm  
BF 1.20 Hz  
RGAIN 27

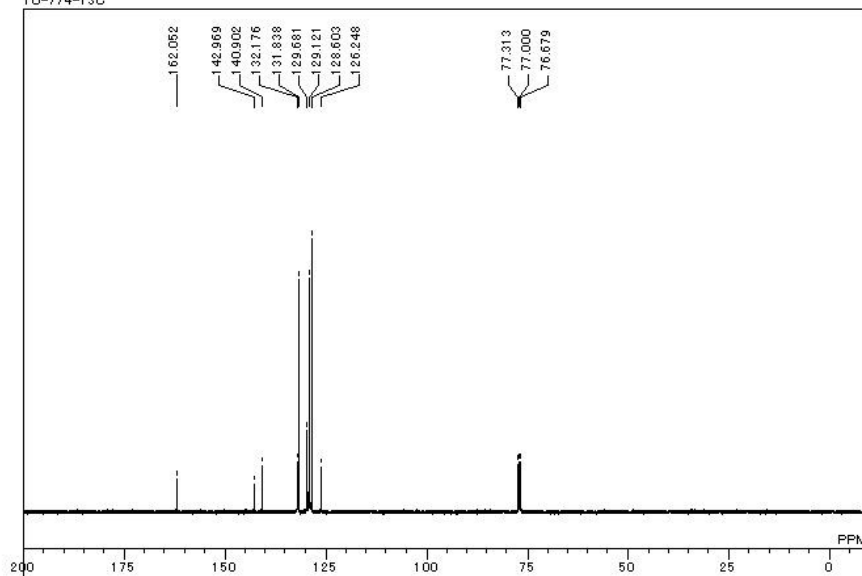
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TU-774



DFILE F:\JADS-Carbonylation NMR\TU-  
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OBNUC 1H  
EXMOD NON  
OBFRQ 399.65 MHz  
OBSET 124.00 KHz  
OBFIN 10500.00 Hz  
POINT 16384  
FREQU 7992.01 Hz  
SCANS 8  
AQTM 2.0500 sec  
PD 4.9500 sec  
PWI 6.20 usec  
IRNUC 1H  
CTEMP 24.0 c  
SLVNT CDCL3  
EXREF 0.00 ppm  
BF 0.12 Hz  
RGAIN 11

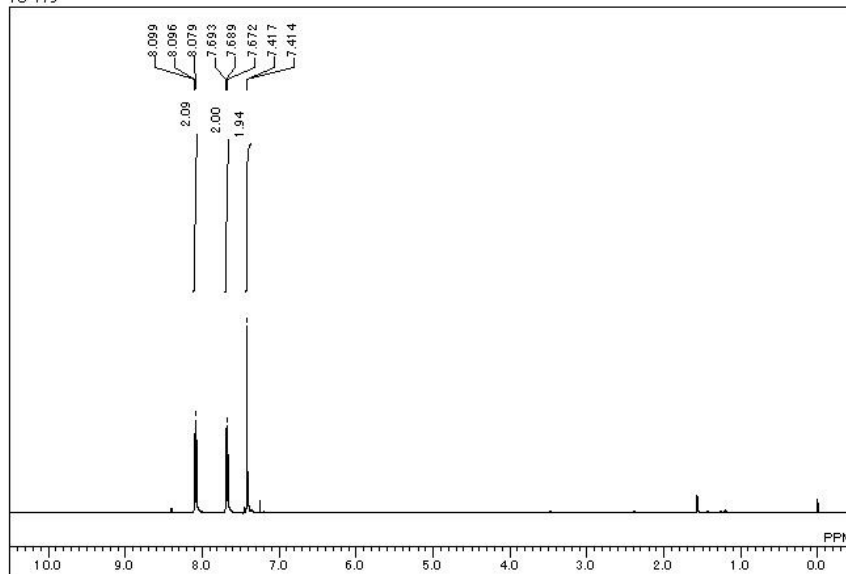


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TU-774-13C

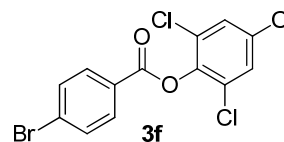


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OBSET 125.00 KHz  
OBFIN 10500.00 Hz  
POINT 32768  
FREQU 27118.64 Hz  
SCANS 128  
AQTM 1.2083 sec  
PD 1.7920 sec  
PWI 5.50 usec  
IRNUC 1H  
CTEMP 24.9 c  
SLVNT CDCL3  
EXREF 77.00 ppm  
BF 1.20 Hz  
RGAIN 26

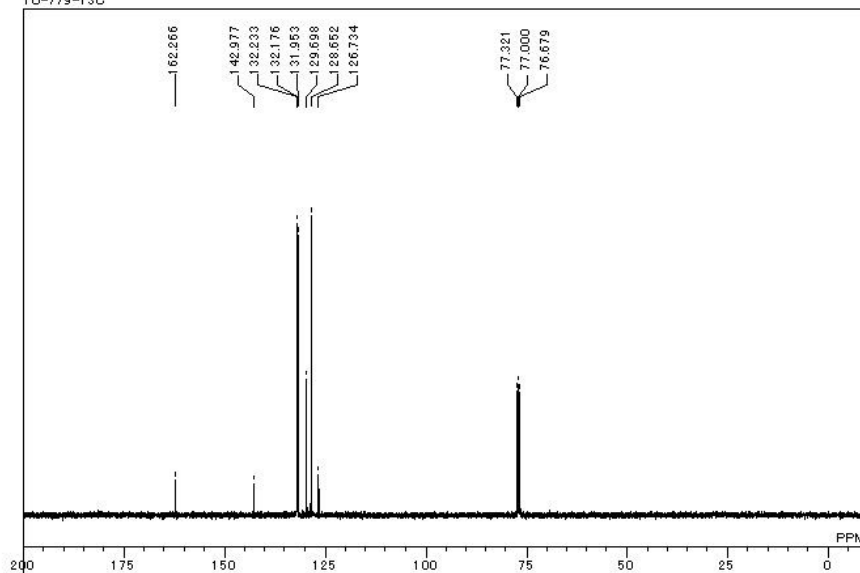
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TU-779



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OBSET 124.00 KHz  
OBFIN 10500.00 Hz  
POINT 16384  
FREQU 7992.01 Hz  
SCANS 8  
AQTM 2.0500 sec  
PD 4.9500 sec  
PWI 6.20 usec  
IRNUC 1H  
CTEMP 24.7 c  
SLVNT CDCL3  
EXREF 0.00 ppm  
BF 0.12 Hz  
RGAIN 13

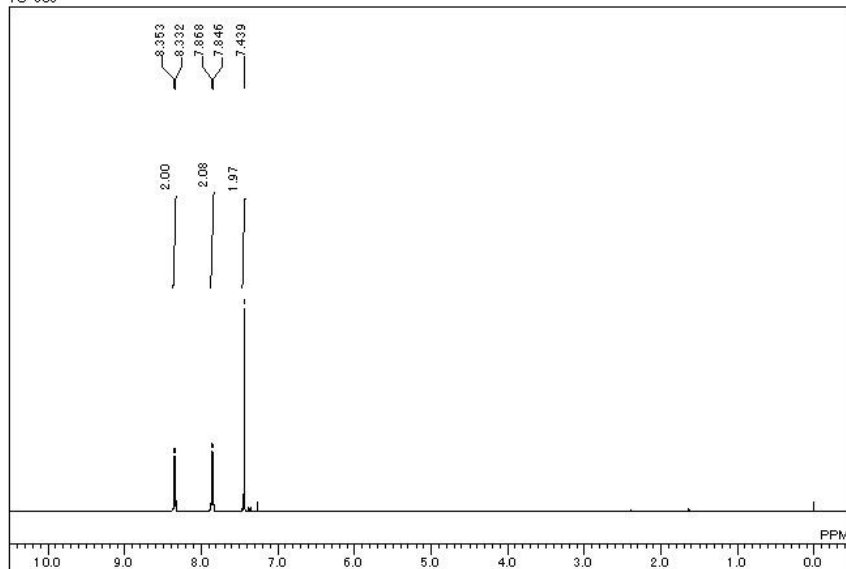


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TU-779-13C

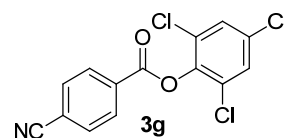


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OBSET 125.00 KHz  
OBFIN 10500.00 Hz  
POINT 32768  
FREQU 27118.64 Hz  
SCANS 128  
AQTM 1.2083 sec  
PD 1.7920 sec  
PWI 5.50 usec  
IRNUC 1H  
CTEMP 25.5 c  
SLVNT CDCL3  
EXREF 77.00 ppm  
BF 1.20 Hz  
RGAIN 28

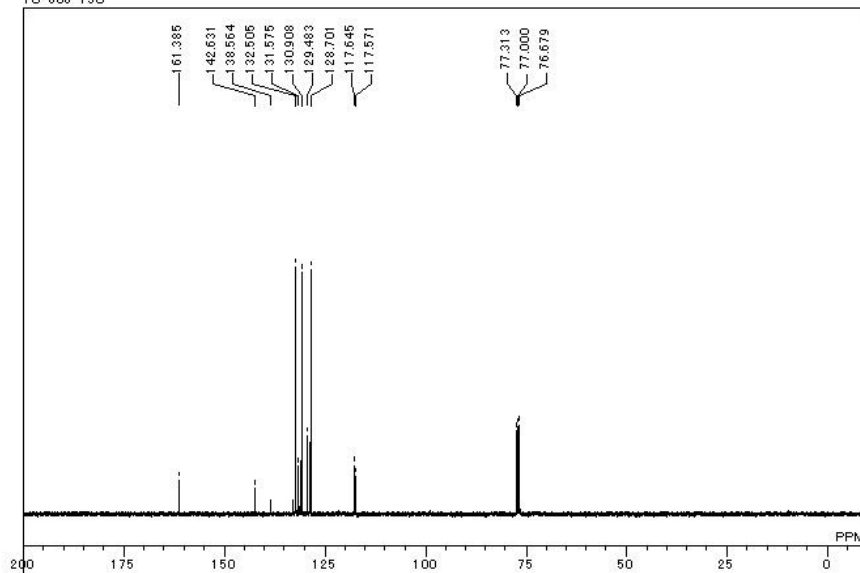
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TU-808



DFILE F:\JACS-Carbonylation NMR\TU-  
COMNT TU-808  
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EXMOD NON  
OBFRO 399.65 MHz  
OBSET 124.00 KHz  
OBFIN 10500.00 Hz  
POINT 16384  
FREQU 7992.01 Hz  
SCANS 8  
AQTM 2.0500 sec  
PD 4.9500 sec  
PWI 6.20 usec  
IRNUC 1H  
CTEMP 24.1 c  
SLVNT CDCL3  
XREF 0.00 ppm  
BF 0.12 Hz  
RGAIN 13

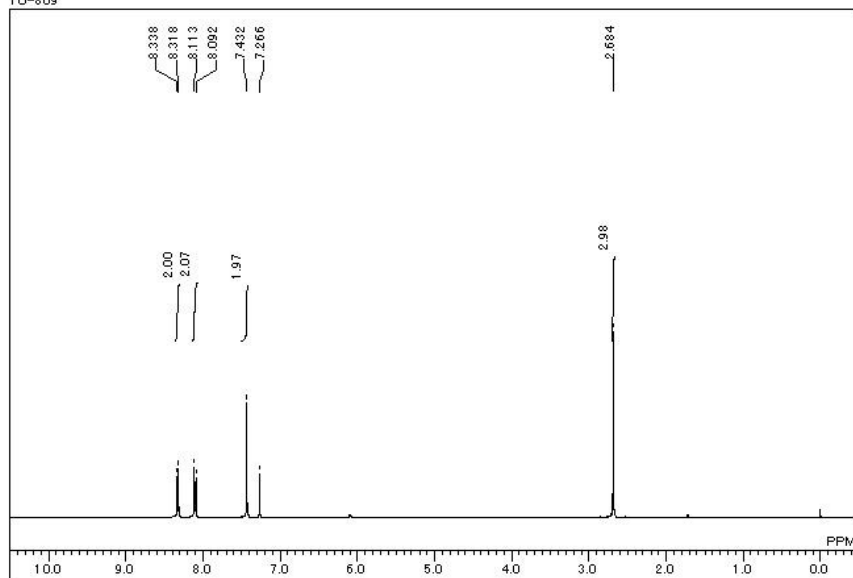


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TU-808-13C

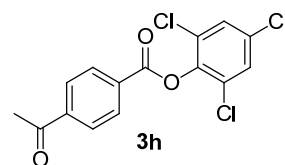


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OBSET 125.00 KHz  
OBFIN 10500.00 Hz  
POINT 32768  
FREQU 27118.64 Hz  
SCANS 128  
AQTM 1.2083 sec  
PD 1.7920 sec  
PWI 5.50 usec  
IRNUC 1H  
CTEMP 24.7 c  
SLVNT CDCL3  
XREF 77.00 ppm  
BF 1.20 Hz  
RGAIN 26

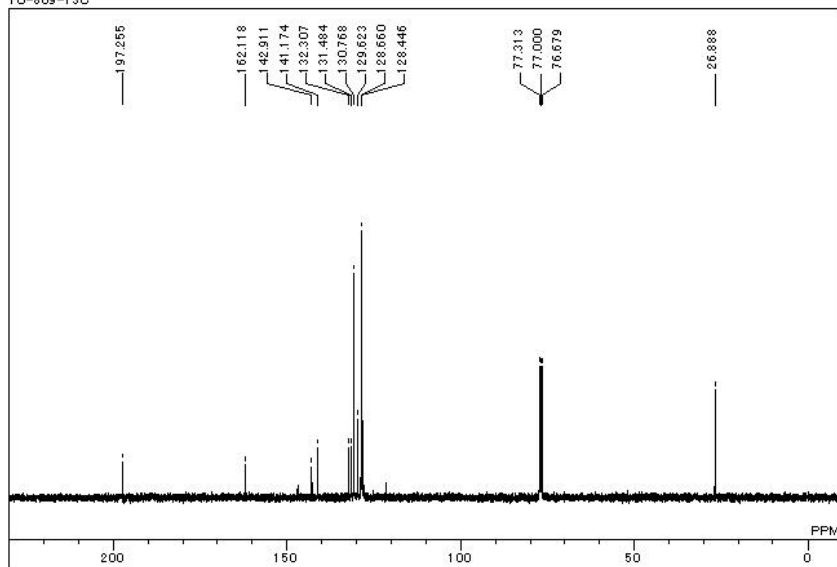
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TU-809



DFILE F:\JACS-Carbonylation NMR\TU-8091NONJE16\_FT.als  
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EXMOD NDN  
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OBSET 124.00 KHz  
OBFIN 10500.00 Hz  
POINT 16384  
FREQU 7992.01 Hz  
SCANS 8  
ACQTM 2.0500 sec  
PD 4.9500 sec  
PWI 6.20 usec  
IRNUC 1H  
CTEMP 24.1 °C  
SLVNT CDCL3  
EXREF 0.00 ppm  
BF 0.12 Hz  
RGAIN 13

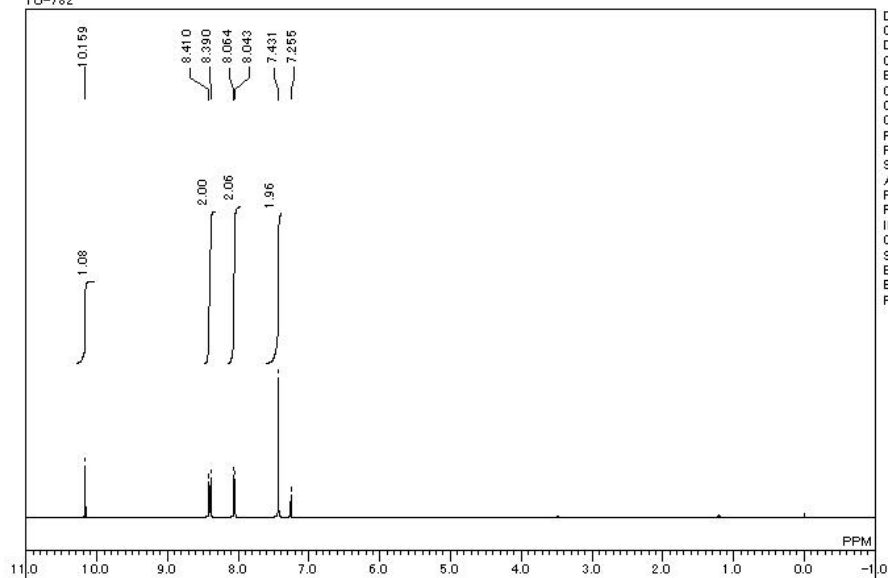


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TU-809-130

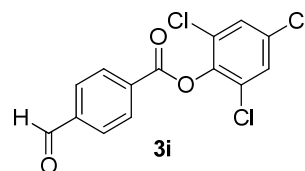


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OBNUC 13C  
EXMOD BCM  
OBFRQ 100.40 MHz  
OBSET 125.00 KHz  
OBFIN 10500.00 Hz  
POINT 32768  
FREQU 27118.64 Hz  
SCANS 128  
ACQTM 1.2083 sec  
PD 1.7920 sec  
PWI 5.50 usec  
IRNUC 1H  
CTEMP 24.5 °C  
SLVNT CDCL3  
EXREF 77.00 ppm  
BF 1.20 Hz  
RGAIN 28

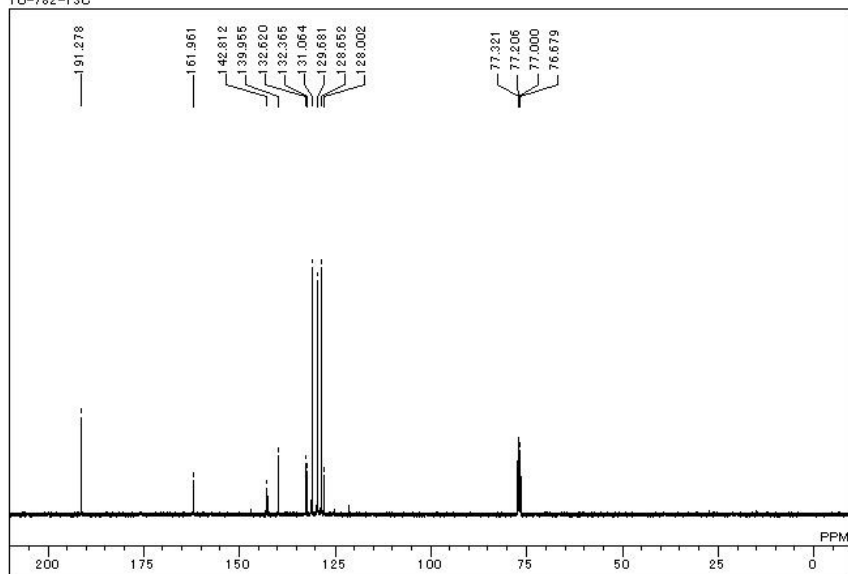
F:\JACS-Carbonylation NMR\TU-7821NON.E20.FT.als  
TU-782



DFILE F:\JACS-Carbonylation NMR\TU-  
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QBNUC 1H  
EXMOD NDN  
OBFRQ 399.65 MHz  
OBSET 124.00 KHz  
OBFIN 10500.00 Hz  
POINT 16384  
FREQU 7992.01 Hz  
SCANS 8  
AQTM 2.0500 sec  
PD 4.9500 sec  
PWI 6.20 usec  
IRNUC 1H  
CTEMP 24.5 c  
SLVNT CDCL3  
EXREF 0.00 ppm  
BF 0.12 Hz  
RGAIN 12

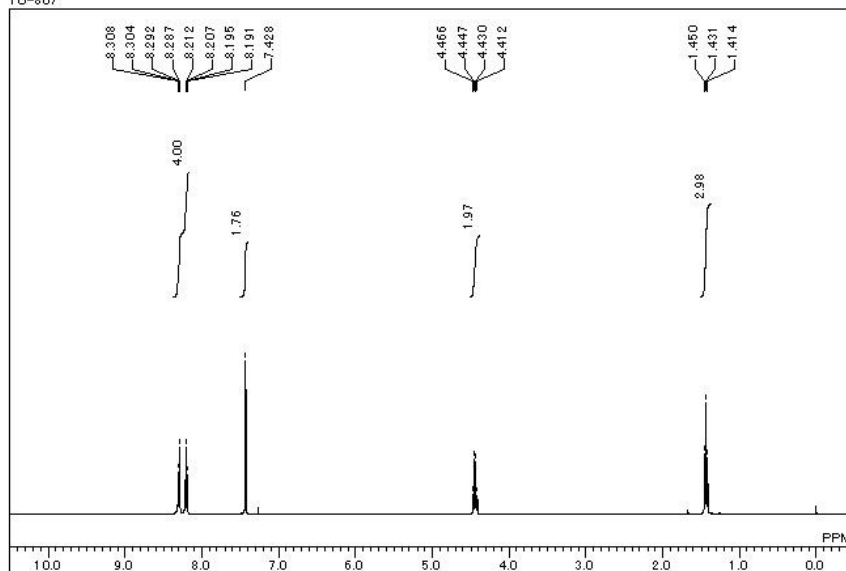


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TU-782-13C

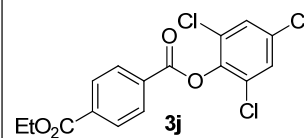


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POINT 32768  
FREQU 27118.64 Hz  
SCANS 128  
AQTM 1.2083 sec  
PD 1.7920 sec  
PWI 5.50 usec  
IRNUC 1H  
CTEMP 24.7 c  
SLVNT CDCL3  
EXREF 77.00 ppm  
BF 1.20 Hz  
RGAIN 26

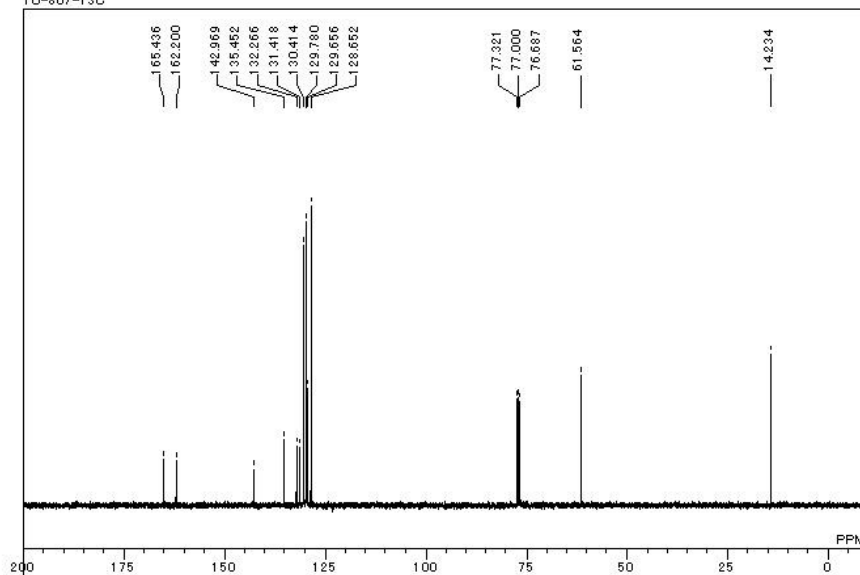
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TU-807



DFILE F:\JACS-Carboxylation NMR\TU-  
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OBNUC 1H  
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OBFREQ 399.65 MHz  
OBSET 124.00 KHz  
OBFIN 10500.00 Hz  
POINT 16384  
FREQ 7992.01 Hz  
SCANS 8  
AQTM 2.0500 sec  
PD 4.9500 sec  
PWI 6.20 usec  
IRNUC 1H  
CTEMP 25.2 °C  
SLVNT CDCL3  
EXREF 0.00 ppm  
BF 0.12 Hz  
RGAIN 11



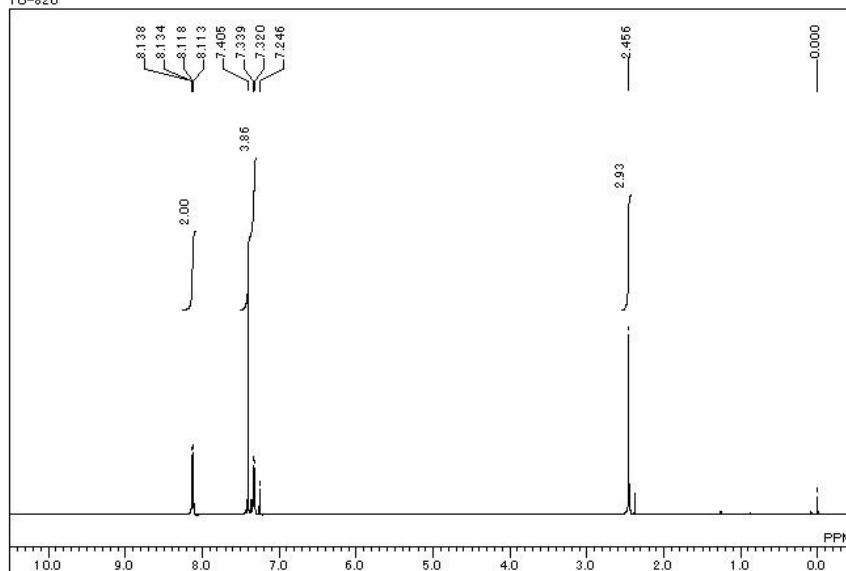
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TU-807-13C



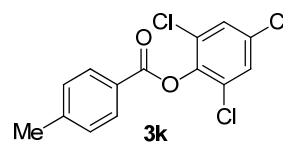
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OBFIN 10500.00 Hz  
POINT 32768  
FREQ 27118.64 Hz  
SCANS 128  
AQTM 1.2083 sec  
PD 1.7920 sec  
PWI 5.50 usec  
IRNUC 1H  
CTEMP 26.1 °C  
SLVNT CDCL3  
EXREF 77.00 ppm  
BF 1.20 Hz  
RGAIN 26



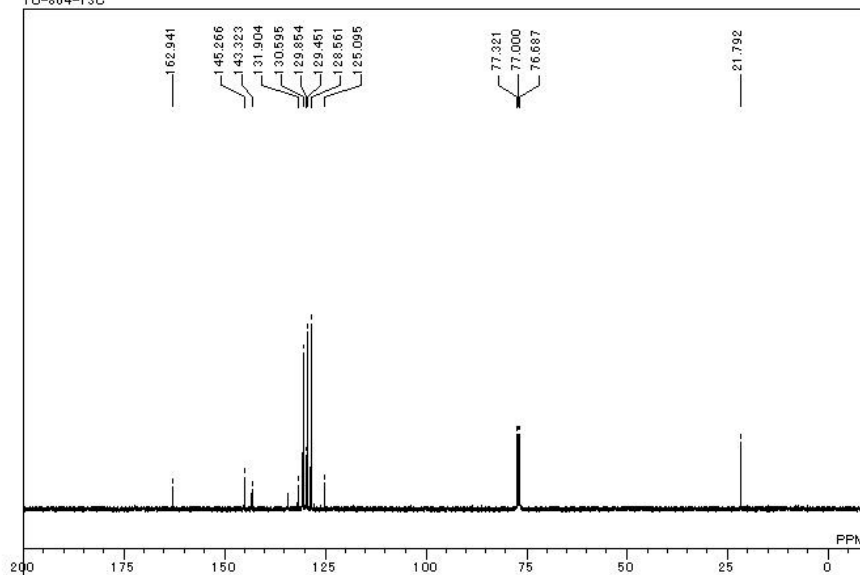
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TU-820



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OBFIN 10500.00 Hz  
POINT 16384  
FREQU 7992.01 Hz  
SCANS 8  
AQGTM 2.0500 sec  
PD 4.9500 sec  
PWI 6.20 usec  
IRNUC 1H  
CTEMP 24.9 c  
SLVNT CDCL3  
EXREF 0.00 ppm  
BF 0.12 Hz  
RGAIN 12

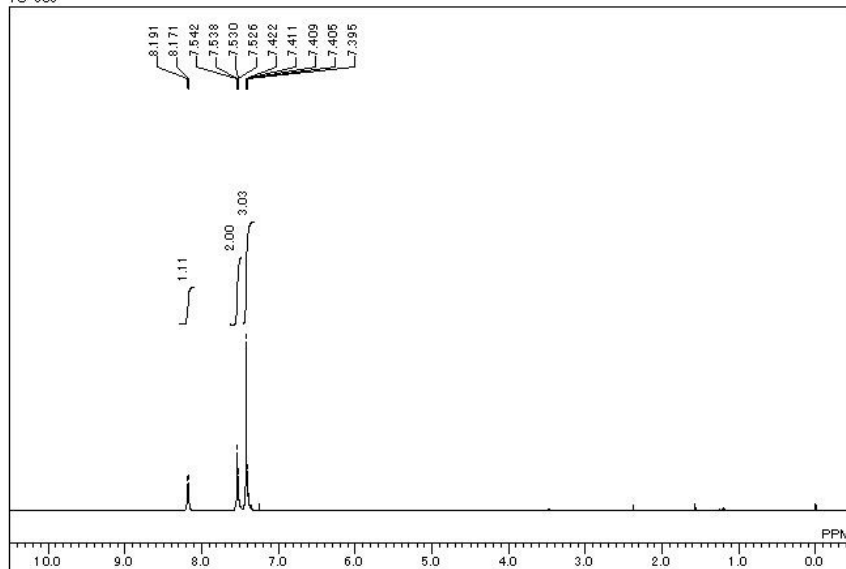


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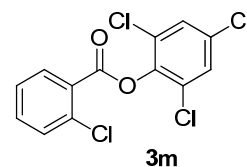


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OBSET 125.00 KHz  
OBFIN 10500.00 Hz  
POINT 32768  
FREQU 27118.64 Hz  
SCANS 128  
AQGTM 1.2083 sec  
PD 1.7920 sec  
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CTEMP 26.3 c  
SLVNT CDCL3  
EXREF 77.00 ppm  
BF 1.20 Hz  
RGAIN 26

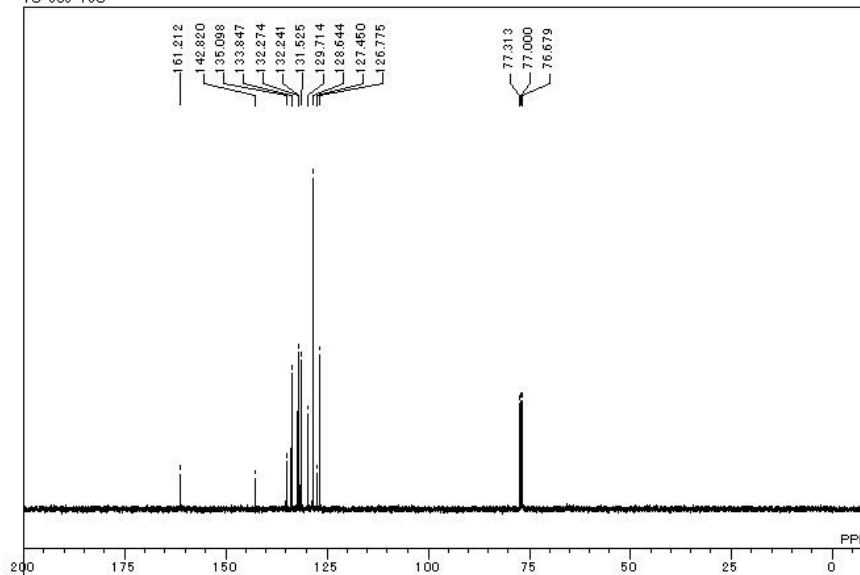
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TU-805



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EXMOD NON  
OBFRO 399.65 MHz  
OBSET 124.00 KHz  
OBFIN 10500.00 Hz  
POINT 16384  
FREQU 7992.01 Hz  
SCANS 8  
ACQTM 2.0500 sec  
PD 4.9500 sec  
PWI 6.20 usec  
IRNUC 1H  
CTEMP 24.4 c  
SLVNT CDCL3  
EXREF 0.00 ppm  
BF 0.12 Hz  
RGAIN 13

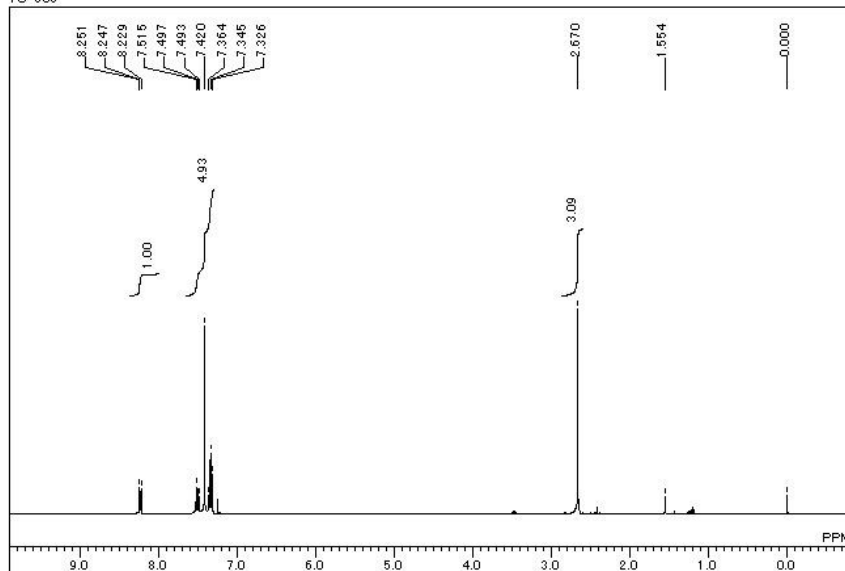


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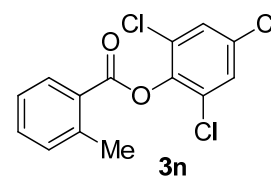


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OBSET 125.00 KHz  
OBFIN 10500.00 Hz  
POINT 32768  
FREQU 27118.64 Hz  
SCANS 128  
ACQTM 1.2083 sec  
PD 1.7920 sec  
PWI 5.50 usec  
IRNUC 1H  
CTEMP 25.1 c  
SLVNT CDCL3  
EXREF 77.00 ppm  
BF 1.20 Hz  
RGAIN 27

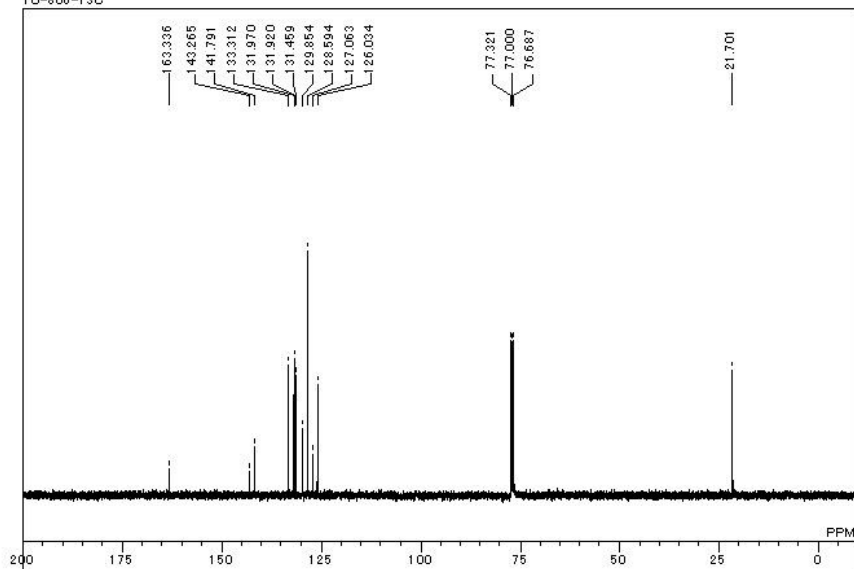
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TU-806



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OBSET 124.00 KHz  
OBFIN 10500.00 Hz  
POINT 16384  
FREQU 7992.01 Hz  
SCANS 8  
AQTM 2.0500 sec  
PD 4.9500 sec  
PWI 6.20 usec  
IRNUC 1H  
CTEMP 23.9 c  
SLVNT CDCL3  
EXREF 0.00 ppm  
BF 0.12 Hz  
RGAIN 13

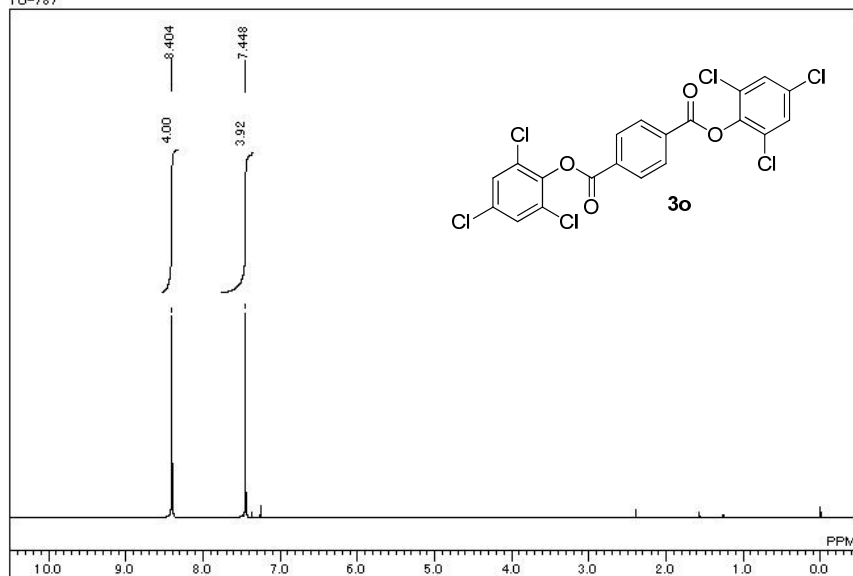


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TU-806-13C



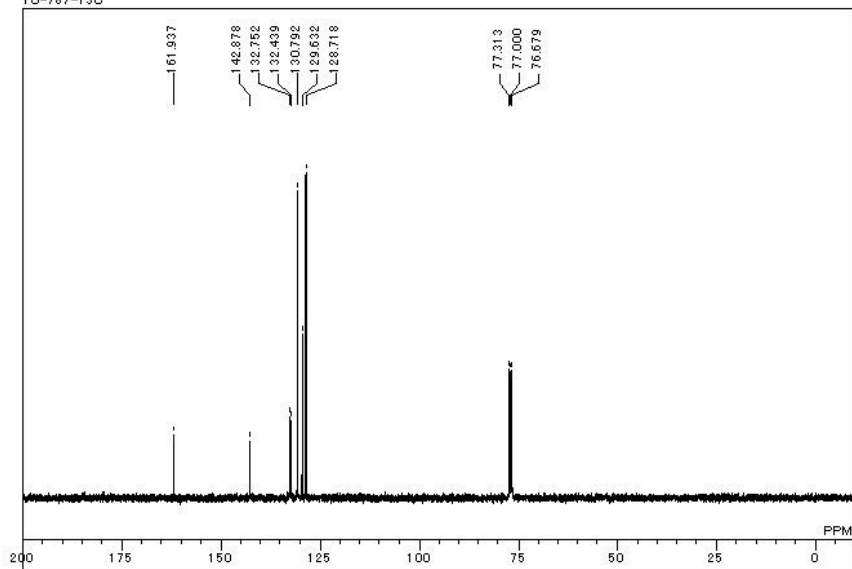
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OBSET 125.00 KHz  
OBFIN 10500.00 Hz  
POINT 32768  
FREQU 27118.64 Hz  
SCANS 128  
AQTM 1.2083 sec  
PD 1.7920 sec  
PWI 5.50 usec  
IRNUC 1H  
CTEMP 24.9 c  
SLVNT CDCL3  
EXREF 77.00 ppm  
BF 1.20 Hz  
RGAIN 28

F:\JACS-Carbonylation NMR\TU-7871NONJE7\_FT.als  
TU-787



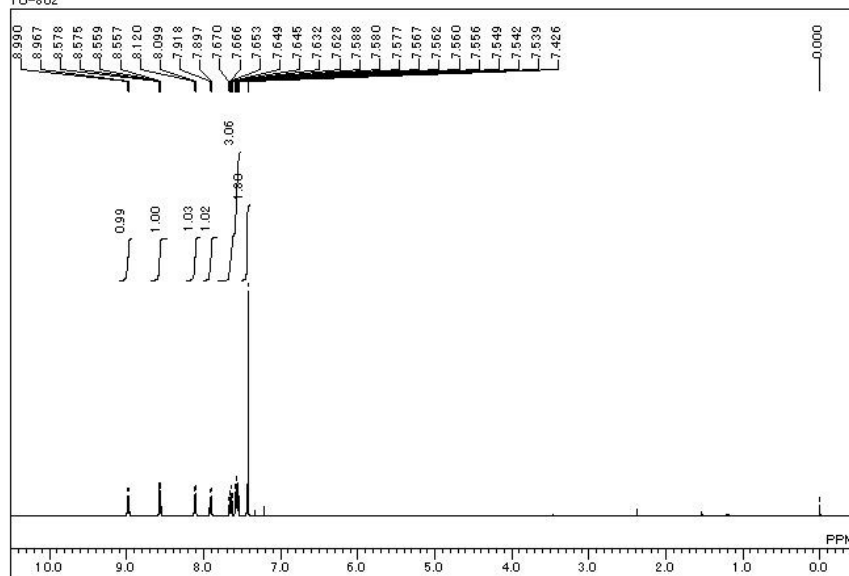
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EXMOD NDN  
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OBSET 124.00 KHz  
OBFIN 10500.00 Hz  
POINT 16384  
FREQU 7992.01 Hz  
SCANS 8  
AQTM 2.0500 sec  
PD 4.9500 sec  
PWI 6.20 usec  
IRNUC 1H  
CTEMP 24.7 c  
SLVNT CDCL3  
EXREF 0.00 ppm  
BF 0.12 Hz  
RGAIN 13

F:\JACS-Carbonylation NMR\TU-787-13C1BCM\_E8\_FT.als  
TU-787-13C

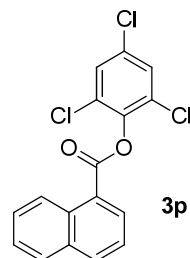


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OBFIN 10500.00 Hz  
POINT 32768  
FREQU 27118.64 Hz  
SCANS 128  
AQTM 1.2083 sec  
PD 1.7920 sec  
PWI 5.50 usec  
IRNUC 1H  
CTEMP 25.5 c  
SLVNT CDCL3  
EXREF 77.00 ppm  
BF 1.20 Hz  
RGAIN 28

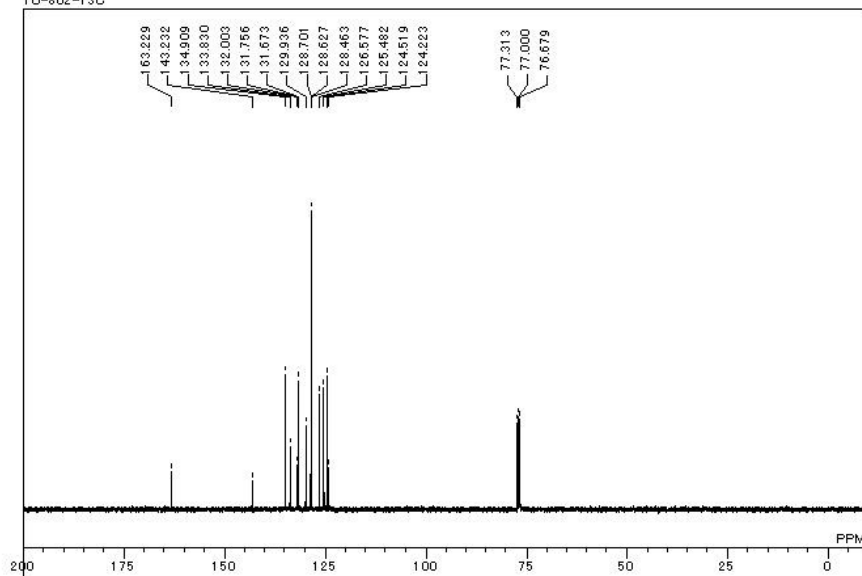
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TU-802



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OBNUC 1H  
EXMOD NON  
OBFRQ 399.65 MHz  
OBSET 124.00 KHz  
OBFIN 10500.00 Hz  
POINT 16384  
FREQU 7992.01 Hz  
SCANS 8  
AQTM 2.0500 sec  
PD 4.9500 sec  
BF 6.20 usec  
IRNUC 1H  
CTEMP 25.4 c  
SLVNT ODCL3  
EXREF 0.00 ppm  
BF 0.12 Hz  
RGAIN 11

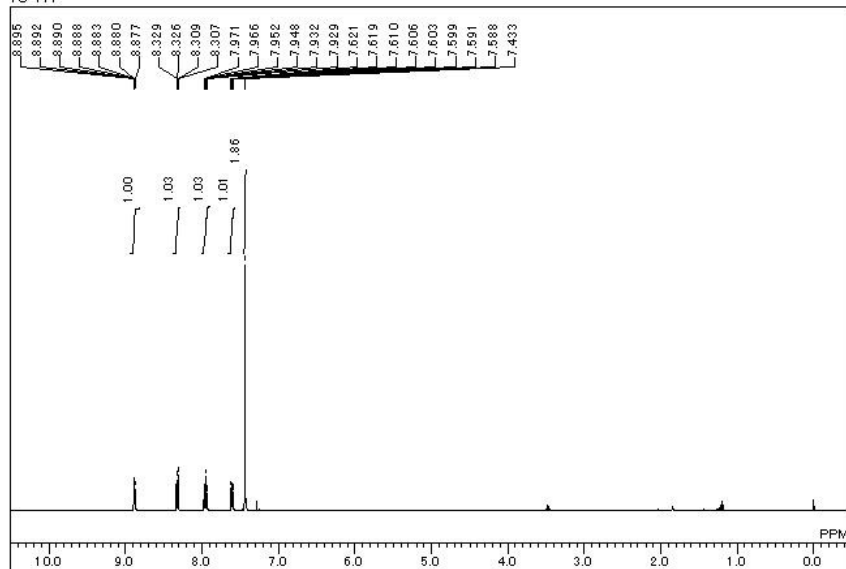


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TU-802-13C

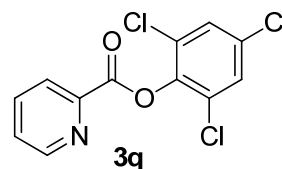


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EXMOD BCM  
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OBSET 125.00 KHz  
OBFIN 10500.00 Hz  
POINT 32768  
FREQU 27118.64 Hz  
SCANS 128  
AQTM 1.2083 sec  
PD 1.7920 sec  
PW 5.50 usec  
IRNUC 1H  
CTEMP 25.2 c  
SLVNT ODCL3  
EXREF 77.00 ppm  
BF 1.20 Hz  
RGAIN 26

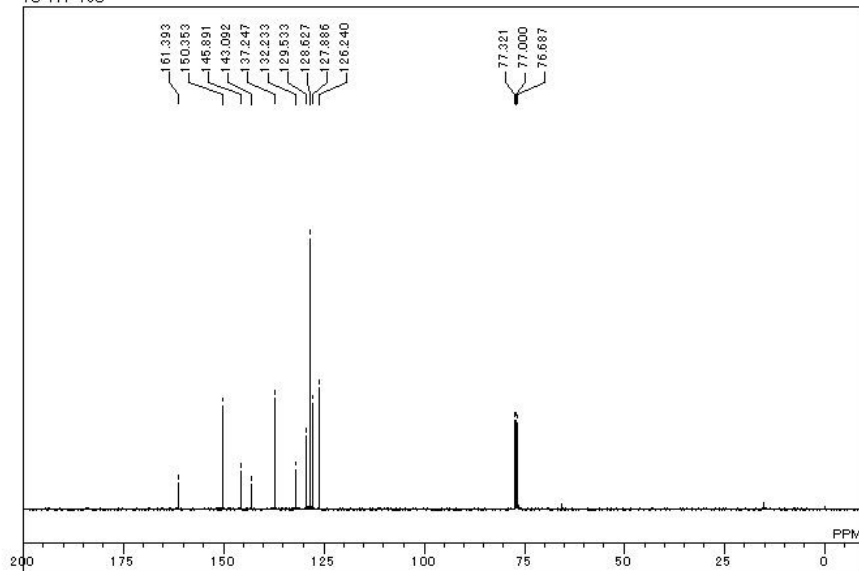
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TU-777



DFILE F:\JACS-Carbonylation NMR\TU-  
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GBNUC 1H  
EXMOD NON  
OBFREQ 399.65 MHz  
OBSET 124.00 KHz  
OBFIN 10500.00 Hz  
POINT 16384  
FREQU 7992.01 Hz  
SCANS 8  
ACQTM 2.0500 sec  
PD 4.9500 sec  
PWI 6.20 usec  
IRNUC 1H  
CTEMP 24.0 c  
SLVNT CDCL3  
EXREF 0.00 ppm  
BF 012 Hz  
RGAIN 13

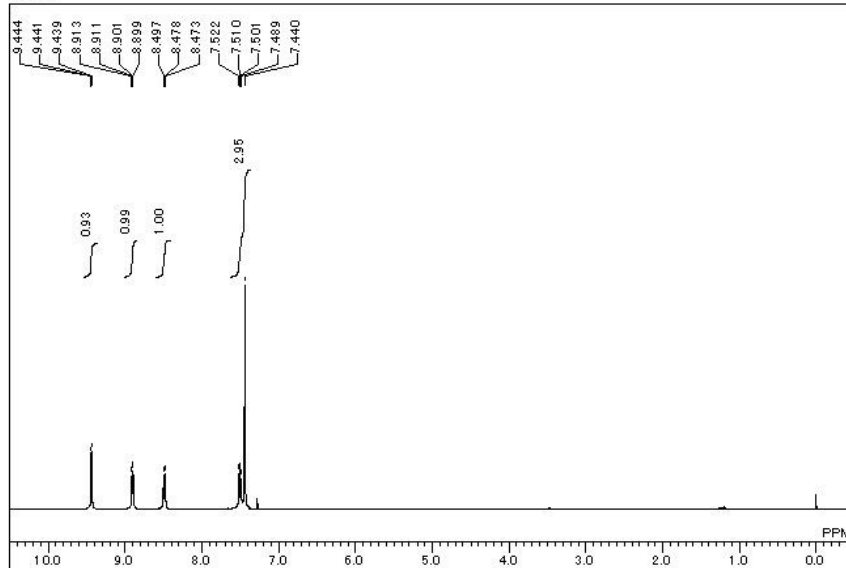


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TU-777-13C

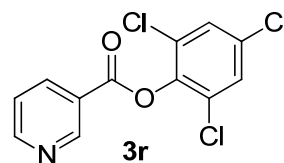


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OBSET 125.00 KHz  
OBFIN 10500.00 Hz  
POINT 32768  
FREQU 27118.64 Hz  
SCANS 1024  
ACQTM 1.2083 sec  
PD 1.7920 sec  
PWI 5.50 usec  
IRNUC 1H  
CTEMP 24.5 c  
SLVNT CDCL3  
EXREF 77.00 ppm  
BF 1.20 Hz  
RGAIN 26

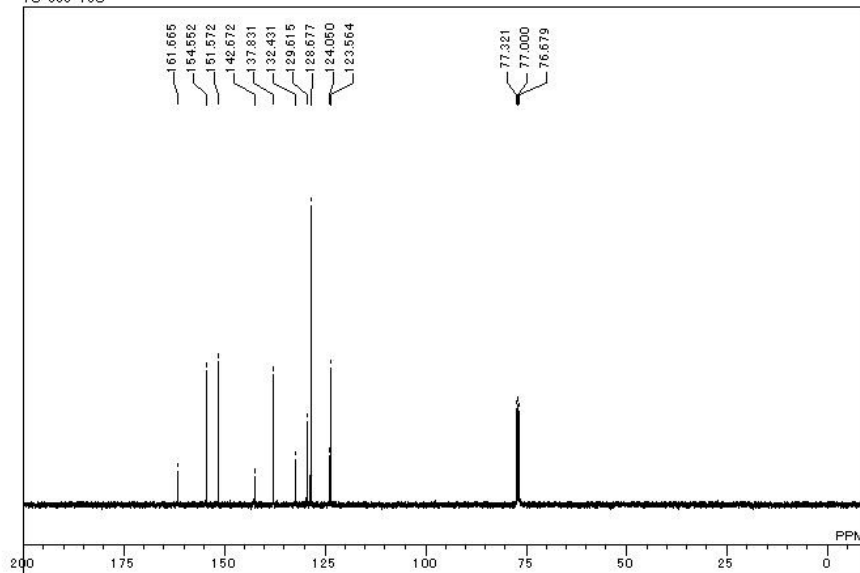
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TU-863



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OBNUC 1H  
EXMOD NON  
OBFRO -399.65 MHz  
OBSET 124.00 KHz  
OBFIN 10500.00 Hz  
POINT 16384  
FREQU 7992.01 Hz  
SCANS 8  
AQTM 2.0500 sec  
PD 4.9500 sec  
PWI 6.20 usec  
IRNUC 1H  
CTEMP 25.5 c  
SLVNT CDCL3  
EXREF 0.00 ppm  
BF 0.12 Hz  
RGAIN 13

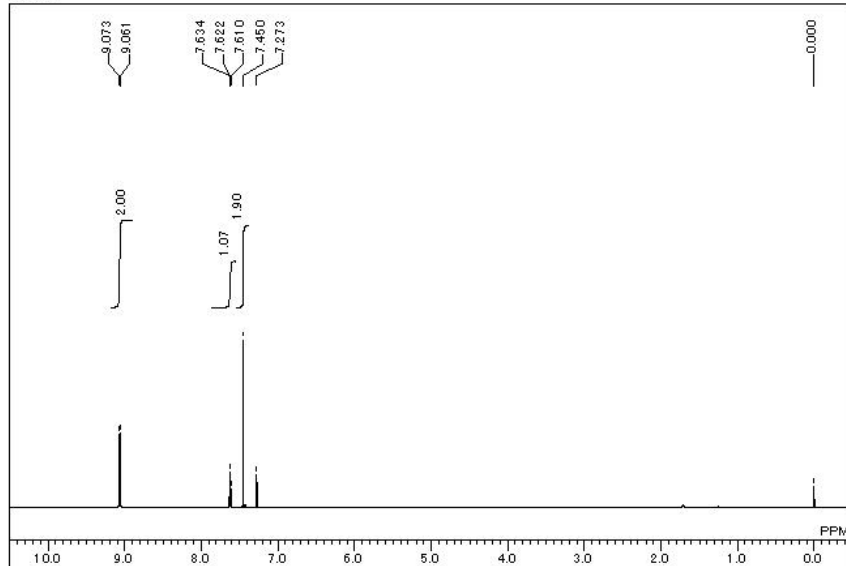


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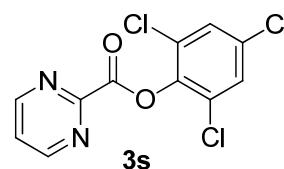


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OBFIN 10500.00 Hz  
POINT 32768  
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SCANS 128  
AQTM 1.2083 sec  
PD 1.7920 sec  
PWI 5.50 usec  
IRNUC 1H  
CTEMP 25.8 c  
SLVNT CDCL3  
EXREF 77.00 ppm  
BF 1.20 Hz  
RGAIN 27

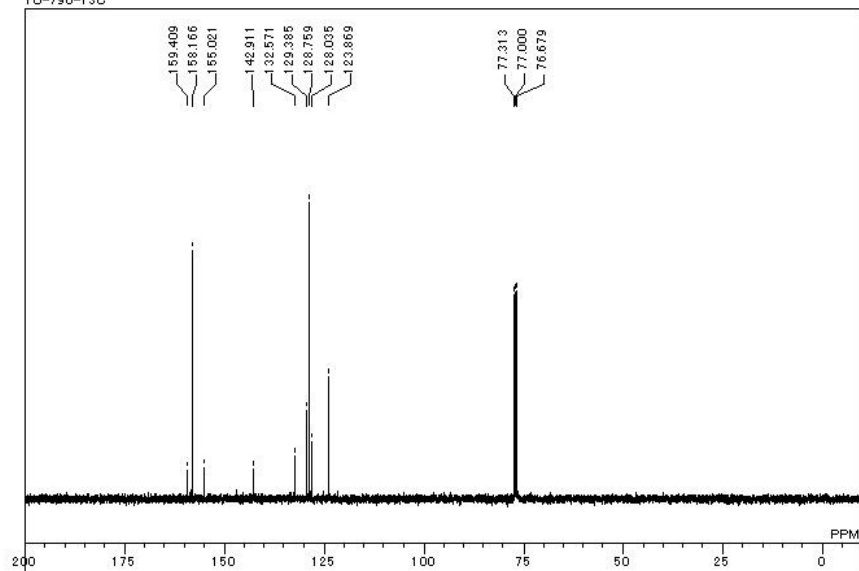
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TU-790



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OBSET 124.00 KHz  
OBFIN 10500.00 Hz  
POINT 16384  
FREQU 7992.01 Hz  
SCANS 8  
AQTM 2.0500 sec  
PD 4.9500 sec  
PWI 6.20 usec  
IRNUC 1H  
CTEMP 24.0 c  
SLVNT CDCL3  
EXREF 0.00 ppm  
BF 012 Hz  
RGAIN 15



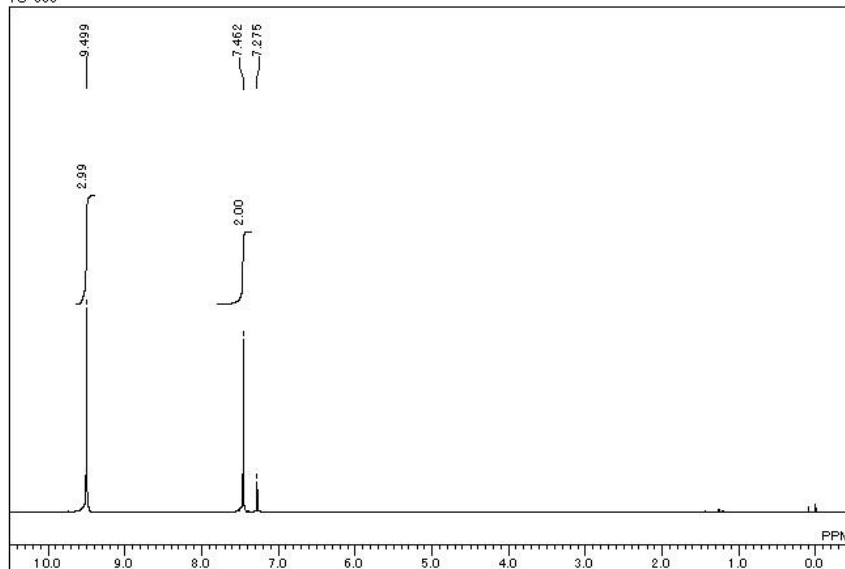
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TU-790-13C



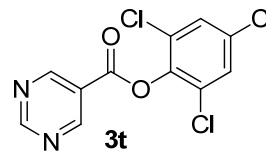
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OBSET 125.00 KHz  
OBFIN 10500.00 Hz  
POINT 32768  
FREQU 27118.64 Hz  
SCANS 128  
AQTM 1.2083 sec  
PD 1.7920 sec  
PWI 5.50 usec  
IRNUC 1H  
CTEMP 25.5 c  
SLVNT CDCL3  
EXREF 77.00 ppm  
BF 120 Hz  
RGAIN 26



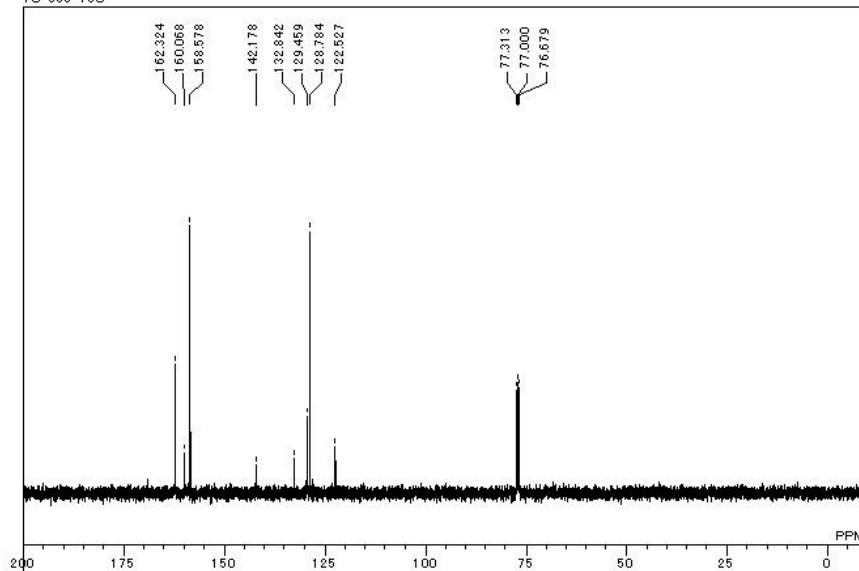
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TU-866



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EXMOD NON  
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OBSET 124.00 KHz  
OBFIN 10500.00 Hz  
POINT 16384  
FREQU 7992.01 Hz  
SCANS 8  
AQTM 2.0500 sec  
PD 4.9500 sec  
PWI 6.20 usec  
IRNUC 1H  
CTEMP 24.7 c  
SLVNT CDCL3  
EXREF 0.00 ppm  
BF 0.12 Hz  
RGAIN 13

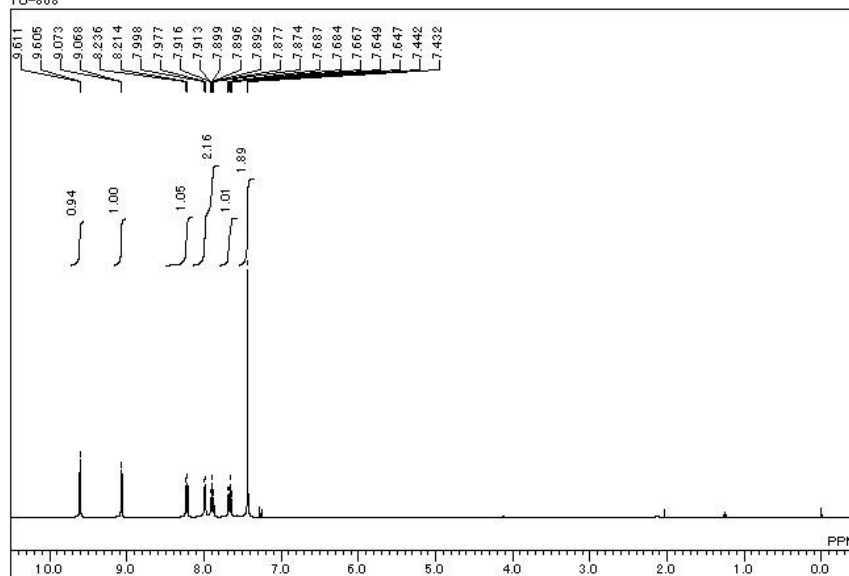


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TU-866-13C

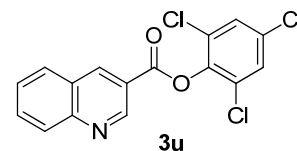


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OBFIN 10500.00 Hz  
POINT 32768  
FREQU 27118.64 Hz  
SCANS 16  
AQTM 1.2083 sec  
PD 1.7920 sec  
PWI 5.50 usec  
IRNUC 1H  
CTEMP 27.2 c  
SLVNT CDCL3  
EXREF 77.00 ppm  
BF 1.20 Hz  
RGAIN 28

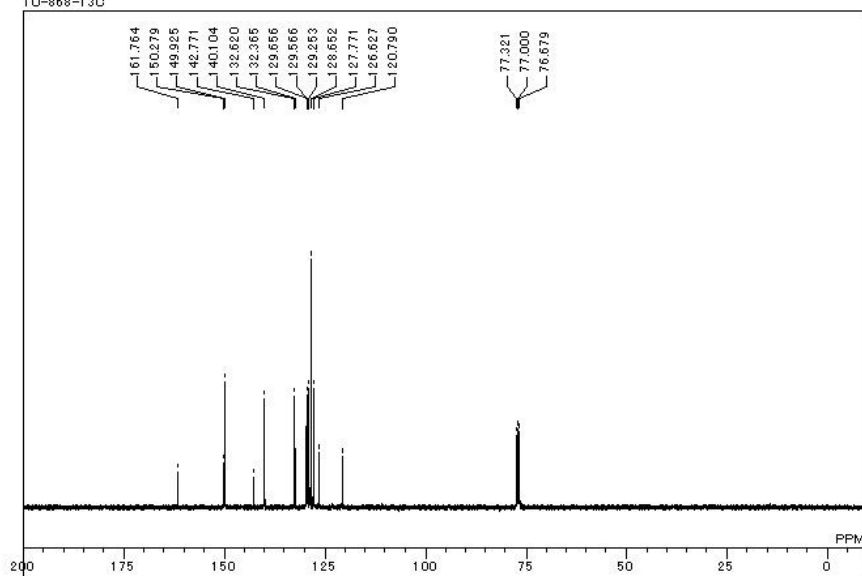
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TU-868



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EXMOD NDN  
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OBSET 124.00 KHz  
OBFIN 10500.00 Hz  
POINT 16384  
FREQU 7992.01 Hz  
SCANS 8  
AQTM 2.0500 sec  
PD 4.9500 sec  
PWI 6.20 usec  
IRNUC 1H  
CTEMP 26.3 c  
SLVNT CDCL3  
EXREF 0.00 ppm  
BF 0.12 Hz  
RGAIN 12

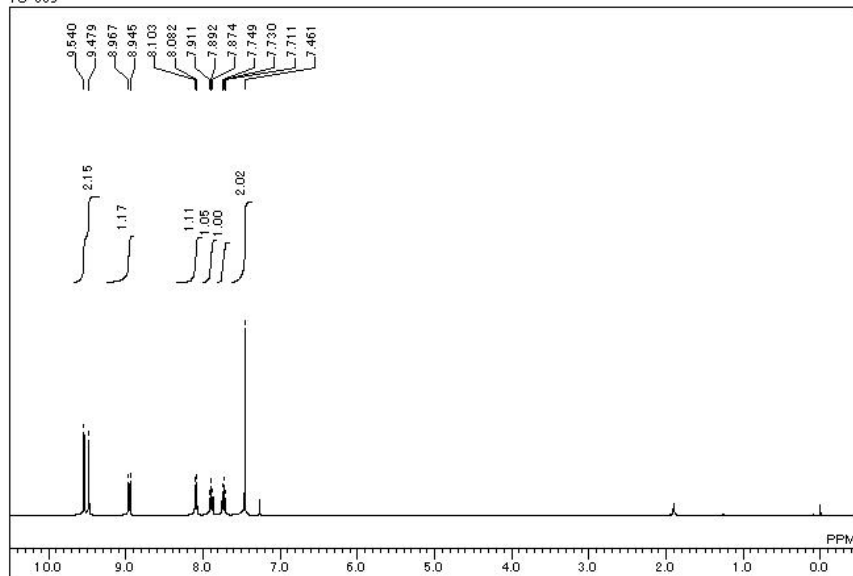


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TU-868-13C

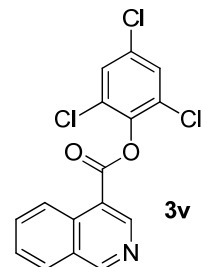


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OBFIN 10500.00 Hz  
POINT 32768  
FREQU 27118.64 Hz  
SCANS 128  
AQTM 1.2083 sec  
PD 1.7920 sec  
PWI 5.50 usec  
IRNUC 1H  
CTEMP 26.3 c  
SLVNT CDCL3  
EXREF 77.00 ppm  
BF 1.20 Hz  
RGAIN 26

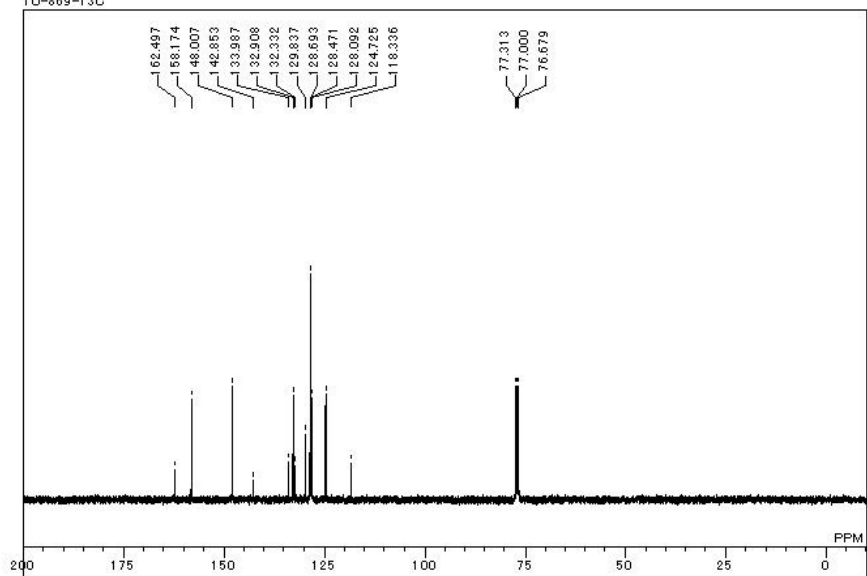
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TU-869



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EXMOD NDN  
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OBSET 124.00 KHz  
OBFIN 10500.00 Hz  
POINT 16384  
FREQU 7992.01 Hz  
SCANS 8  
ACQTM 2.0500 sec  
PD 4.9500 sec  
PWI 6.20 usec  
IRNUC 1H  
CTEMP 26.5 c  
SLVNT CDCL3  
EXREF 0.00 ppm  
BF 0.12 Hz  
RGAIN 13

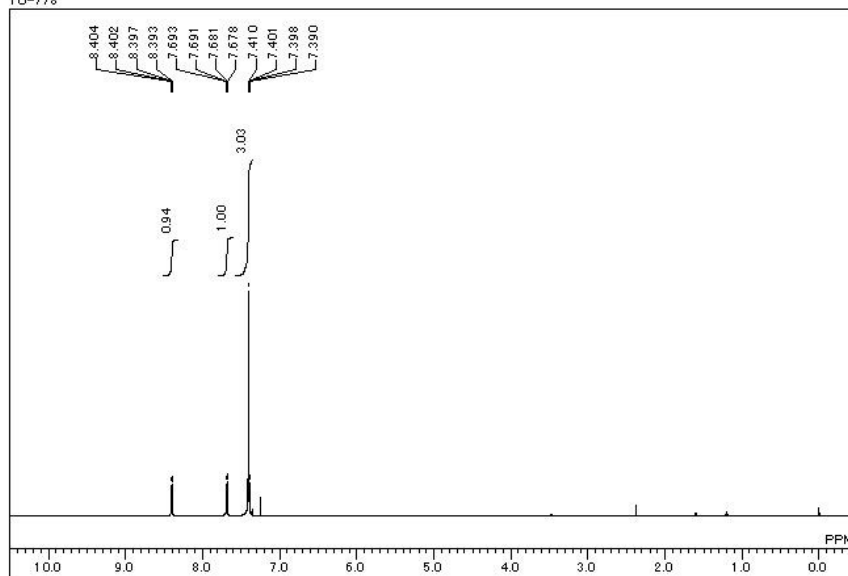


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TU-869-13C

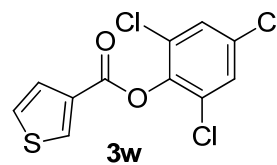


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OBSET 125.00 KHz  
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POINT 32768  
FREQU 27118.64 Hz  
SCANS 128  
ACQTM 1.2083 sec  
PD 1.7920 sec  
PWI 5.50 usec  
IRNUC 1H  
CTEMP 27.7 c  
SLVNT CDCL3  
EXREF 77.00 ppm  
BF 1.20 Hz  
RGAIN 26

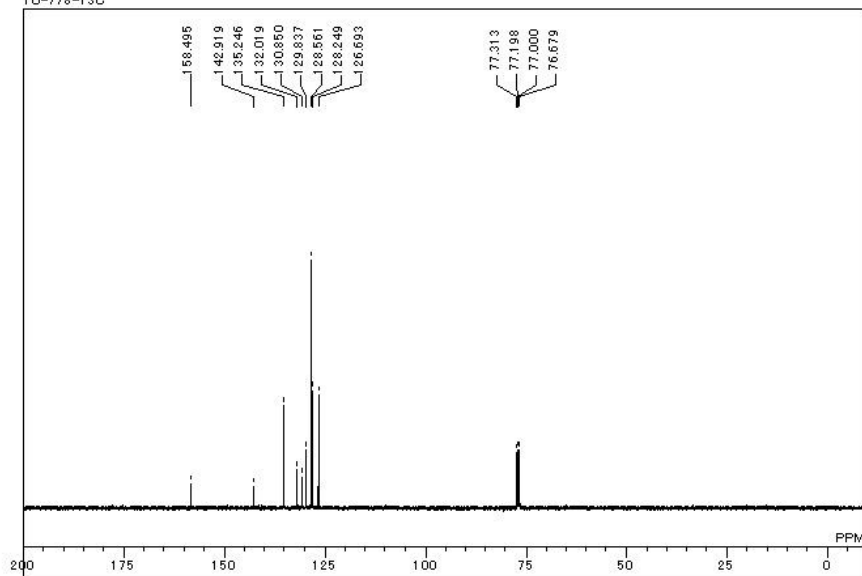
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TU-778



DFILE F:\JACS-Carbonylation NMR\TU-  
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EXMOD NON  
OBFRQ 399.65 MHz  
OBSET 124.00 KHz  
OBFIN 10500.00 Hz  
POINT 16384  
FREQU 7992.01 Hz  
SCANS 8  
AQTM 2.0500 sec  
PD 4.9500 sec  
PWI 6.20 usec  
IRNUC 1H  
CTEMP 24.7 c  
SLVNT CDCL3  
EXREF 0.00 ppm  
BF 0.12 Hz  
RGAIN 12

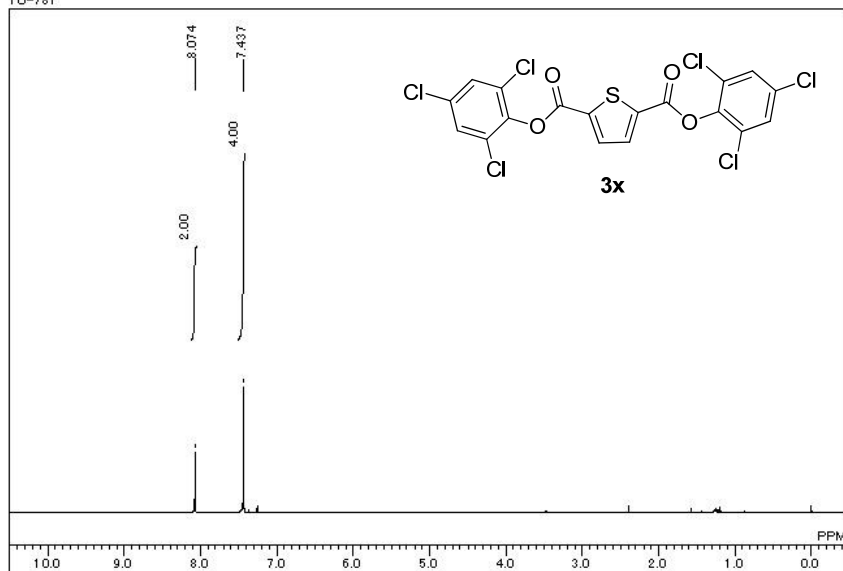


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TU-778-13C



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DATIM Fri Jun 22 10:33:01 2012  
QBNUC 13C  
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OBSET 125.00 KHz  
OBFIN 10500.00 Hz  
POINT 32768  
FREQU 27118.64 Hz  
SCANS 128  
AQTM 1.2083 sec  
PD 1.7920 sec  
PWI 5.50 usec  
IRNUC 1H  
CTEMP 25.5 c  
SLVNT CDCL3  
EXREF 77.00 ppm  
BF 1.20 Hz  
RGAIN 27

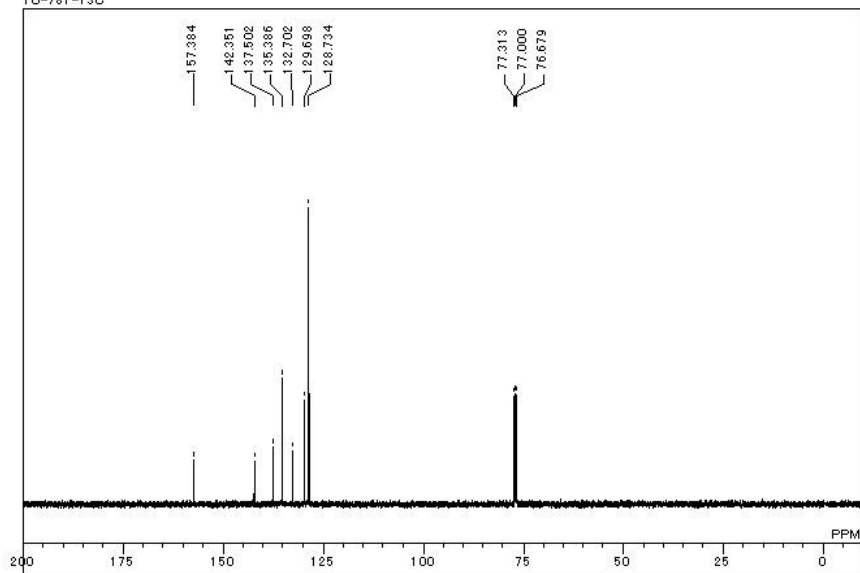
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TU-781



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COMNT  
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OBNUC  
EXMOD  
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OBFIN  
POINT  
FREQU  
SCANS  
ACQTM  
PD  
PWI  
IRNUC  
CTEMP  
SLVNT  
EXREF  
BF  
RGAIN

F:\JACS-Carbonylation NMR\TU-781  
TU-781  
Fri Jun 22 19:14:14 2012  
1H  
NON  
399.65 MHz  
124.00 KHz  
10500.00 Hz  
16384  
7992.01 Hz  
8  
2.0500 sec  
4.9500 sec  
6.20 usec  
1H  
24.4 c  
DDCL3  
0.00 ppm  
0.12 Hz  
15

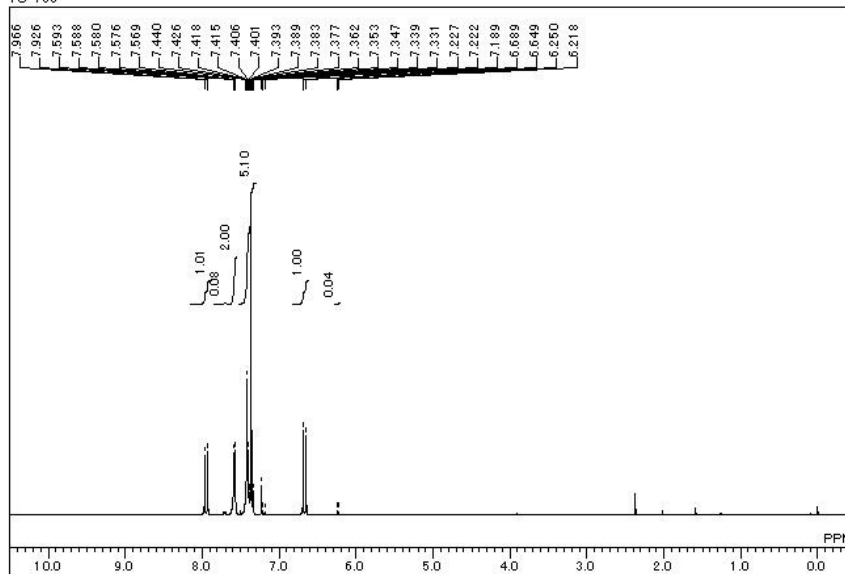
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TU-781-13C



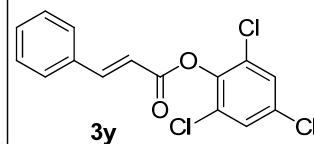
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OBNUC  
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OBSET  
OBFIN  
POINT  
FREQU  
SCANS  
ACQTM  
PD  
PWI  
IRNUC  
CTEMP  
SLVNT  
EXREF  
BF  
RGAIN

F:\JACS-Carbonylation NMR\TU-781-13C  
TU-781-13C  
Fri Jun 22 19:23:33 2012  
13C  
BOM  
100.40 MHz  
125.00 KHz  
10500.00 Hz  
32768  
27118.64 Hz  
128  
1.2083 sec  
1.7920 sec  
5.50 usec  
1H  
24.7 c  
DDCL3  
77.00 ppm  
1.20 Hz  
28

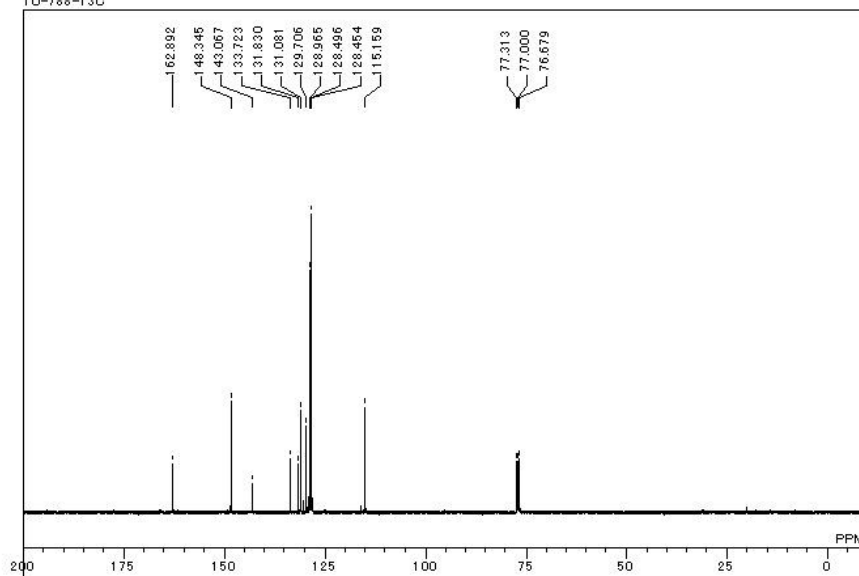
F:\JACS-Carboxylation NMR\TU-7881NON.E3.FT.als  
TU-788



DFILE F:\JACS-Carboxylation NMR\TU-  
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QBNUC 1H  
EXMOD NON  
OBFRQ 399.65 MHz  
OBSET 124.00 KHz  
OBFIN 10500.00 Hz  
POINT 16384  
FREQU 7992.01 Hz  
SCANS 8  
AQTM 2.0500 sec  
PD 4.9500 sec  
PWI 6.20 usec  
IRNUC 1H  
CTEMP 25.1 c  
SLVNT CDCL3  
EXREF 0.00 ppm  
BF 0.12 Hz  
RGAIN 9

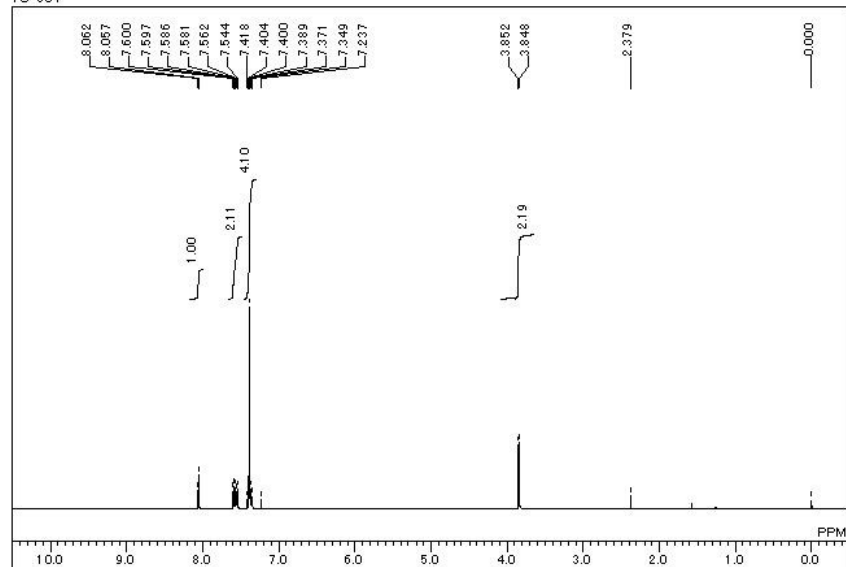


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TU-788-13C

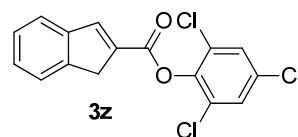


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OBFIN 10500.00 Hz  
POINT 32768  
FREQU 27118.64 Hz  
SCANS 128  
AQTM 1.2083 sec  
PD 1.7920 sec  
PWI 5.50 usec  
IRNUC 1H  
CTEMP 25.5 c  
SLVNT CDCL3  
EXREF 77.00 ppm  
BF 1.20 Hz  
RGAIN 26

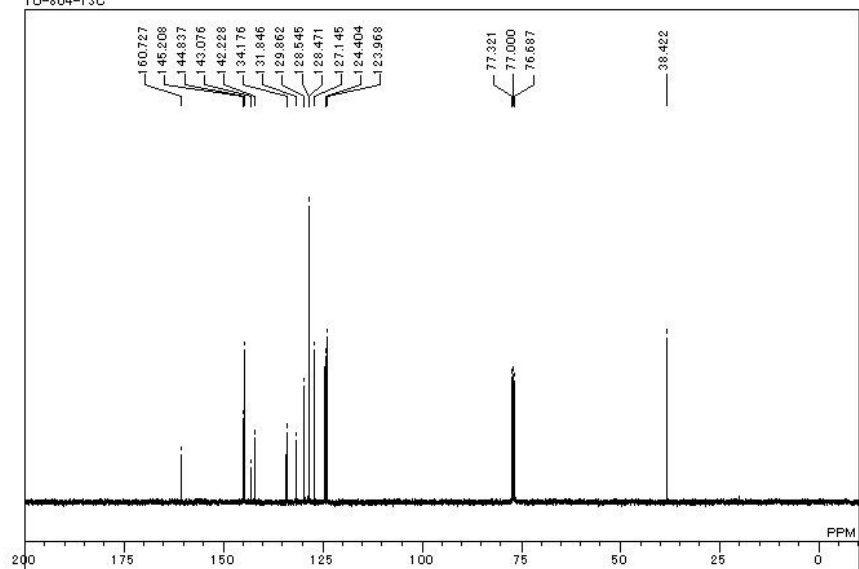
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TU-804



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COMNT TU-804  
DATIM Thu Jun 28 11:53:50 2012  
OBNUC 1H  
EXMOD NON  
OBFRQ 399.65 MHz  
OBSET 124.00 KHz  
OBFIN 10500.00 Hz  
POINT 16384  
FREQU 7992.01 Hz  
SCANS 8  
AQTM 2.0500 sec  
PD 4.9500 sec  
PW 6.20 usec  
IRNUC 1H  
CTEMP 25.2 c  
SLVNT CDCL3  
EXREF 0.00 ppm  
BF 0.12 Hz  
RGAIN 12

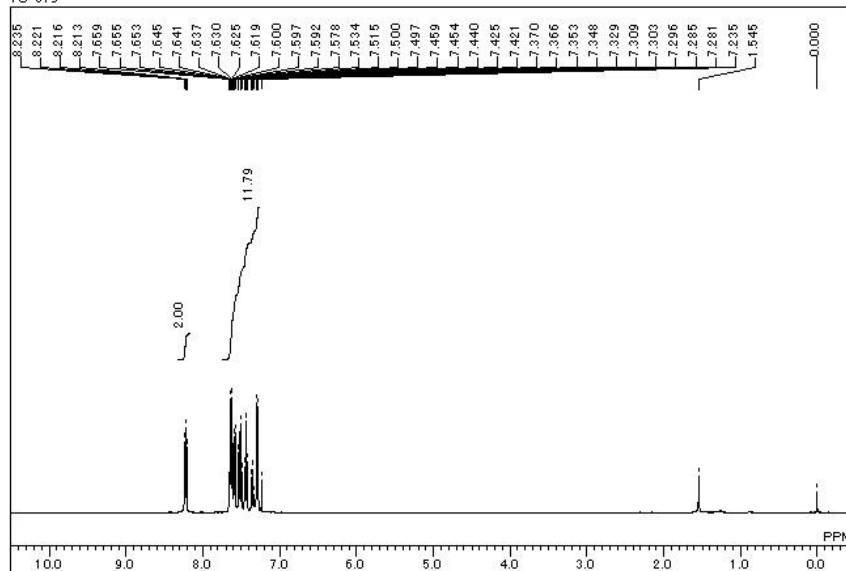


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TU-804-13C

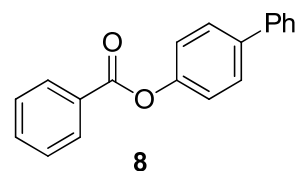


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OBSET 125.00 KHz  
OBFIN 10500.00 Hz  
POINT 32768  
FREQU 27118.64 Hz  
SCANS 128  
AQTM 1.2083 sec  
PD 1.7920 sec  
PW 5.50 usec  
IRNUC 1H  
CTEMP 25.3 c  
SLVNT CDCL3  
EXREF 77.00 ppm  
BF 1.20 Hz  
RGAIN 26

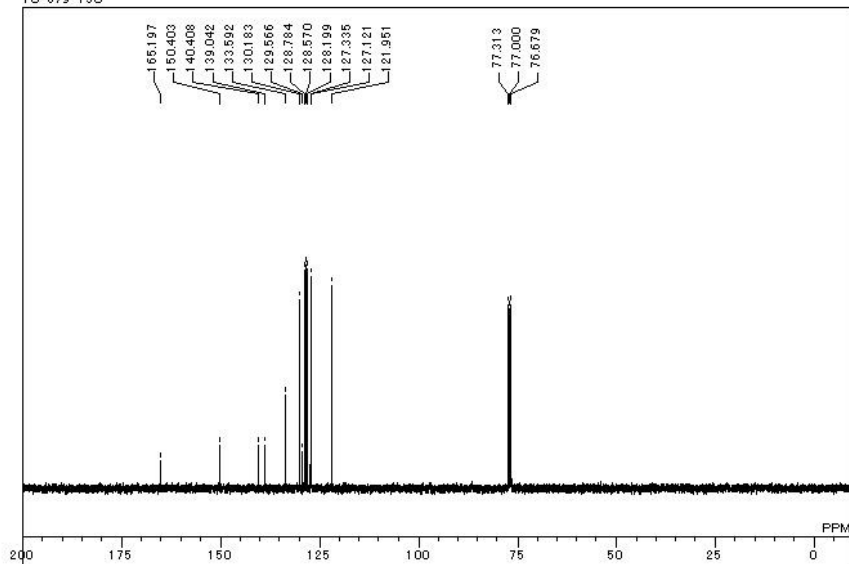
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TU-879



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EXMOD NON  
OBFRO 399.65 MHz  
OBSET 124.00 KHz  
OBFIN 10500.00 Hz  
POINT 16384  
FREQU 7992.01 Hz  
SCANS 8  
AQTM 2.0500 sec  
PD 4.9500 sec  
PWI 6.20 usec  
IRNUC 1H  
CTEMP 29.7 c  
SLVNT CDCL3  
EXREF 0.00 ppm  
BF 0.12 Hz  
RGAIN 13



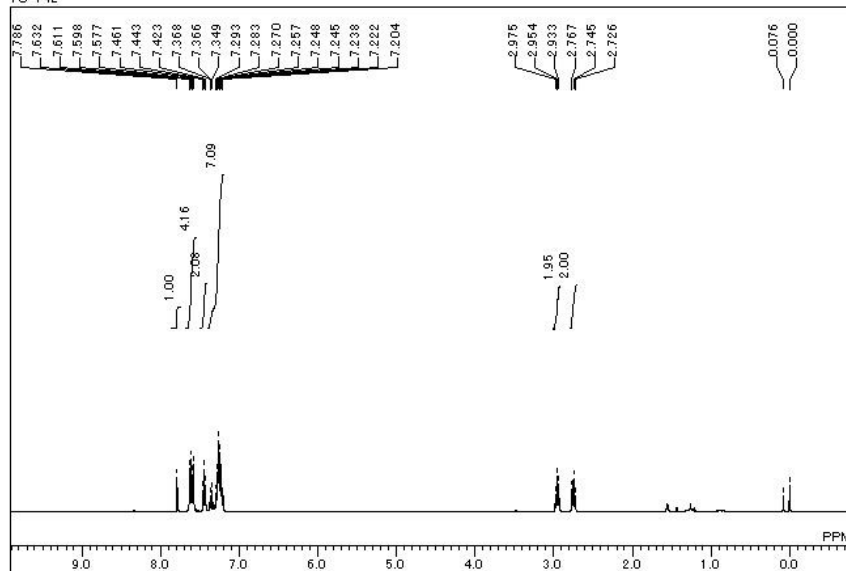
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TU-879-13C



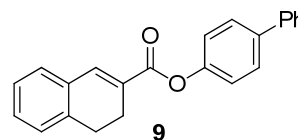
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EXMOD BCM  
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OBSET 125.00 KHz  
OBFIN 10500.00 Hz  
POINT 32768  
FREQU 27118.64 Hz  
SCANS 128  
AQTM 1.2083 sec  
PD 1.7920 sec  
PWI 5.50 usec  
IRNUC 1H  
CTEMP 30.4 c  
SLVNT CDCL3  
EXREF 77.00 ppm  
BF 1.20 Hz  
RGAIN 27



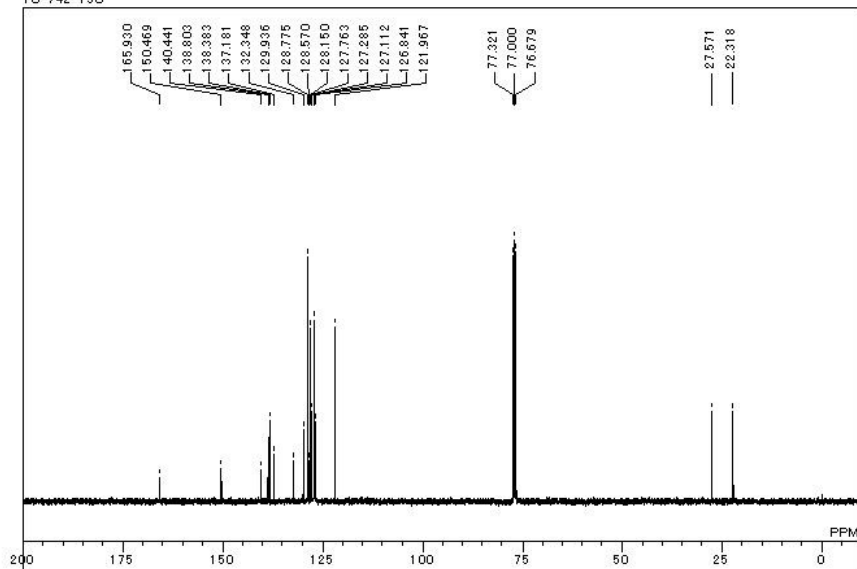
F:\JACS-Carbonylation NMR\TU-7421NONJE9\_FT.als  
TU-742



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OBNUC 1H  
EXMOD NON  
OBFRQ 399.65 MHz  
OBSET 124.00 KHz  
OBFIN 10500.00 Hz  
POINT 16384  
FREQU 7992.01 Hz  
SCANS 8  
ACQTM 2.0500 sec  
PD 4.9500 sec  
PWI 6.20 usec  
IRNUC 1H  
CTEMP 22.9 c  
SLVNT CDCL3  
XREF 0.00 ppm  
BF 0.12 Hz  
RGAIN 13

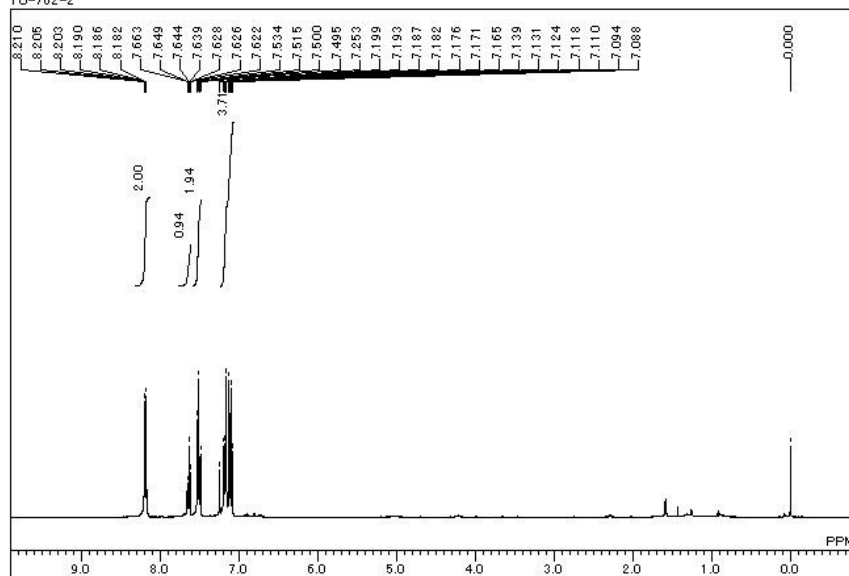


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TU-742-13C

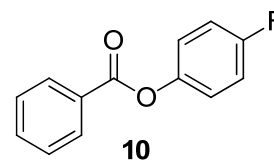


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OBSET 125.00 KHz  
OBFIN 10500.00 Hz  
POINT 32768  
FREQU 27118.64 Hz  
SCANS 512  
ACQTM 1.2083 sec  
PD 1.7920 sec  
PWI 5.50 usec  
IRNUC 1H  
CTEMP 23.9 c  
SLVNT CDCL3  
XREF 77.00 ppm  
BF 1.20 Hz  
RGAIN 26

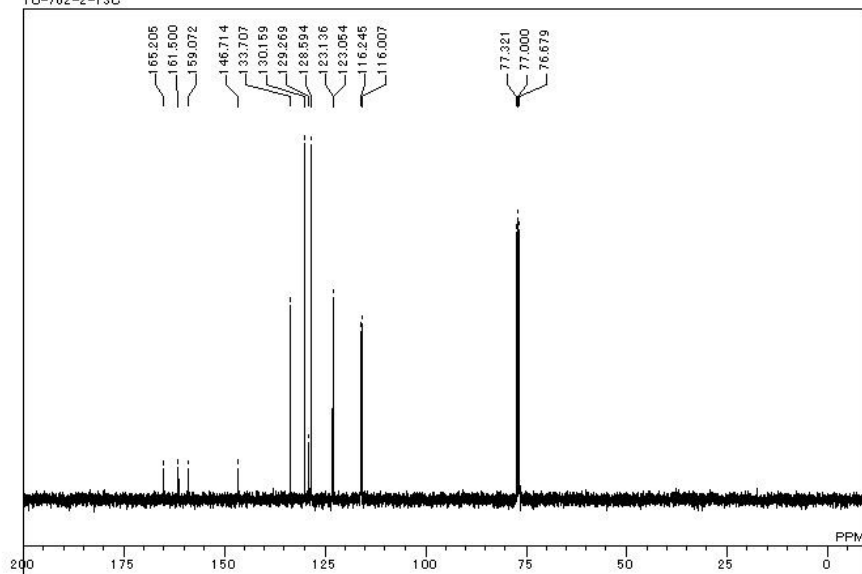
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TU-762-2



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OBSET 124.00 KHz  
OBFIN 10500.00 Hz  
POINT 16384  
FREQU 7992.01 Hz  
SCANS 8  
AQTM 2.0500 sec  
PD 4.9500 sec  
PWI 6.20 usec  
IRNUC 1H  
CTEMP 22.1 °C  
SLVNT CDCL3  
EXREF 0.00 ppm  
BF 0.12 Hz  
RGAIN 13

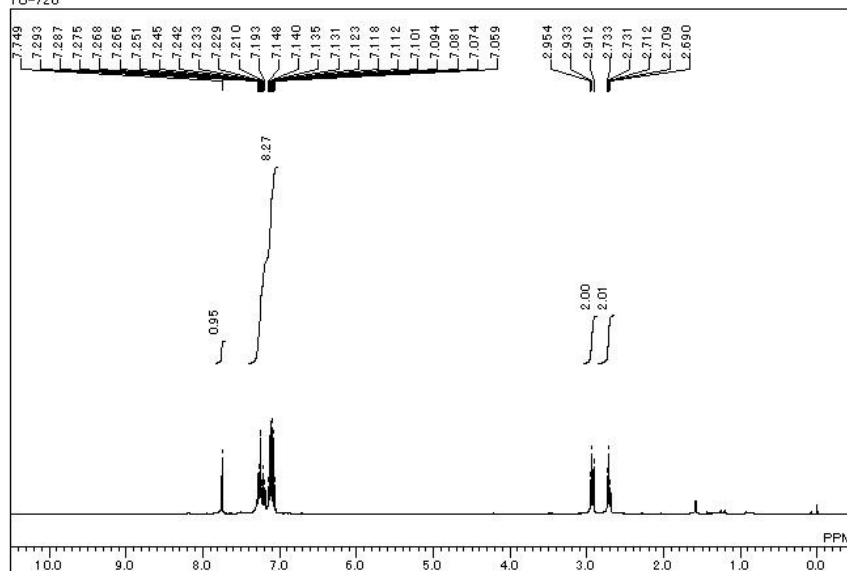


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TU-762-2-13C

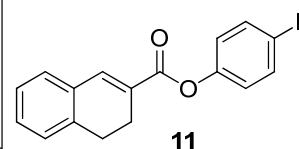


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OBSET 125.00 KHz  
OBFIN 10500.00 Hz  
POINT 32768  
FREQU 27118.64 Hz  
SCANS 128  
AQTM 1.2083 sec  
PD 1.7920 sec  
PWI 5.50 usec  
IRNUC 1H  
CTEMP 23.1 °C  
SLVNT CDCL3  
EXREF 77.00 ppm  
BF 1.20 Hz  
RGAIN 26

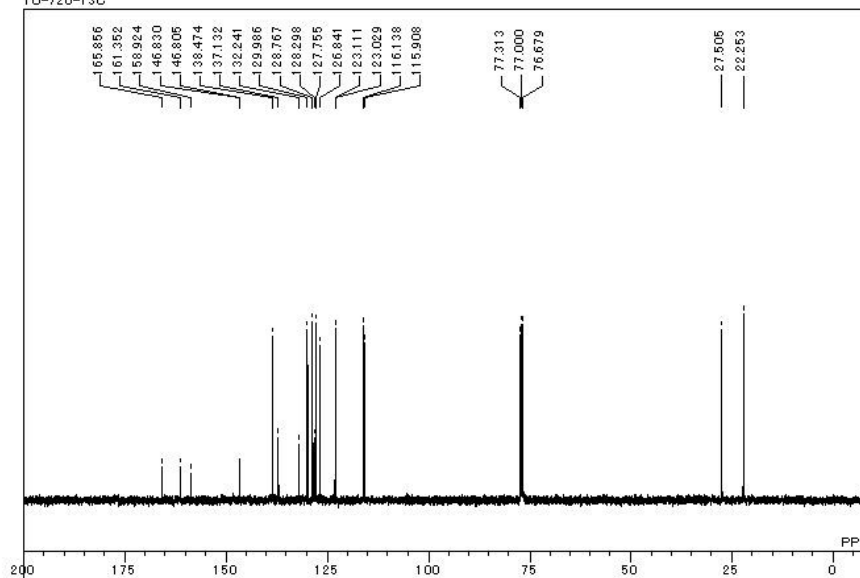
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TU-720



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OBNUC 1H  
EXMOD NON  
OBFRQ 399.65 MHz  
OBSET 124.00 KHz  
OBFIN 10500.00 Hz  
POINT 16384  
FREQU 7992.01 Hz  
SCANS 8  
AQTM 2.0500 sec  
PD 4.9500 sec  
PWI 6.20 usec  
IRNUC 1H  
CTEMP 22.4 c  
SLVNT CDCL3  
EXREF 0.00 ppm  
BF 0.12 Hz  
RGAIN 11

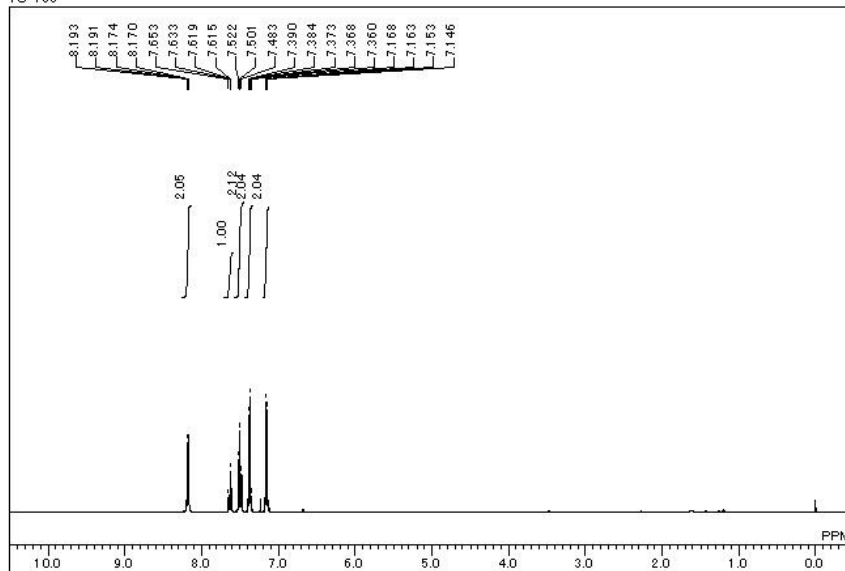


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TU-720-13C

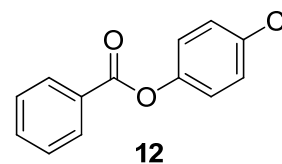


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OBSET 125.00 KHz  
OBFIN 10500.00 Hz  
POINT 32768  
FREQU 27118.64 Hz  
SCANS 128  
AQTM 1.2083 sec  
PD 1.7920 sec  
PWI 5.50 usec  
IRNUC 1H  
CTEMP 23.3 c  
SLVNT CDCL3  
EXREF 77.00 ppm  
BF 1.20 Hz  
RGAIN 26

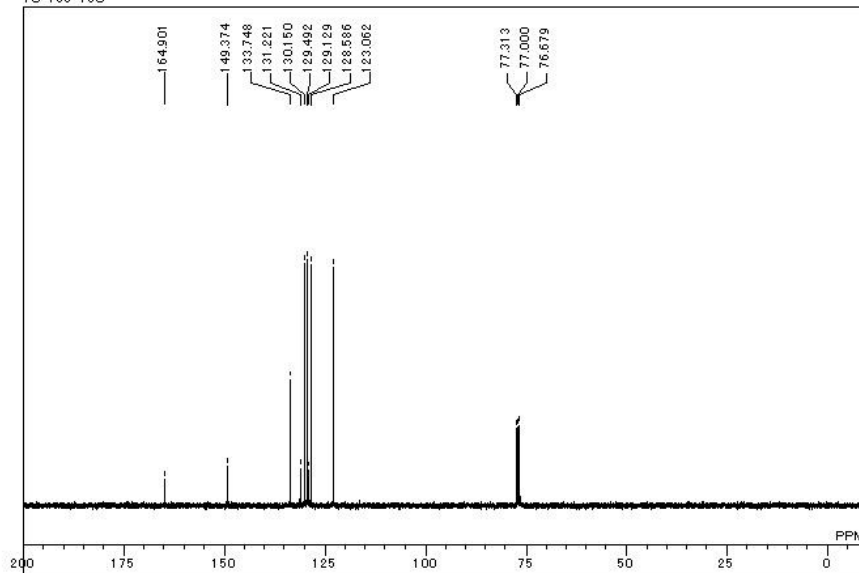
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TU-763



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EXMOD NON  
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OBSET 124.00 KHz  
OBFIN 10500.00 Hz  
POINT 16384  
FREQU 7992.01 Hz  
SCANS 8  
AQTM 2.0500 sec  
PD 4.9500 sec  
PWI 6.20 usec  
IRNUC 1H  
CTEMP 22.5 c  
SLVNT CDCL3  
EXREF 0.00 ppm  
BF 0.12 Hz  
RGAIN 10

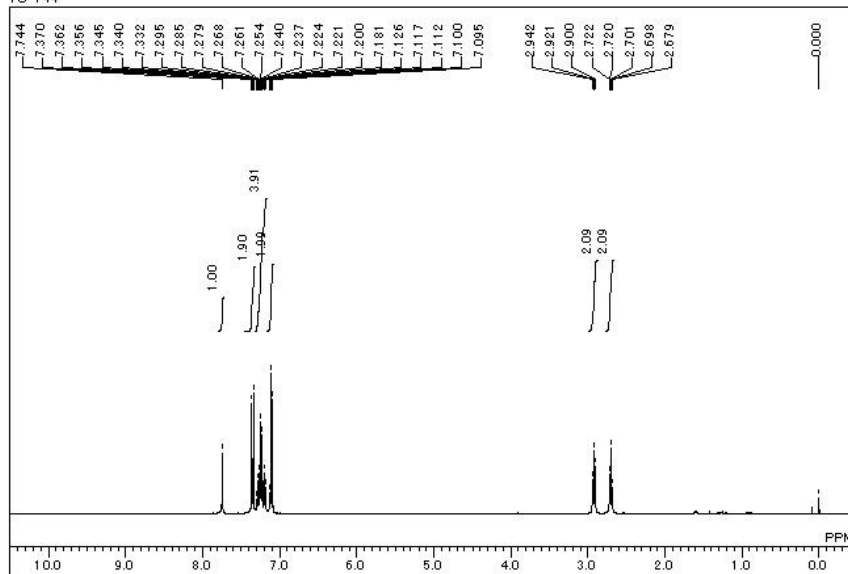


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TU-763-13C

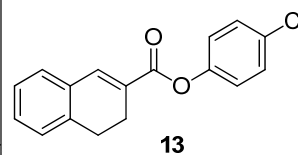


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OBFIN 10500.00 Hz  
POINT 32768  
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SCANS 128  
AQTM 1.2083 sec  
PD 1.7920 sec  
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IRNUC 1H  
CTEMP 23.1 c  
SLVNT CDCL3  
EXREF 77.00 ppm  
BF 1.20 Hz  
RGAIN 26

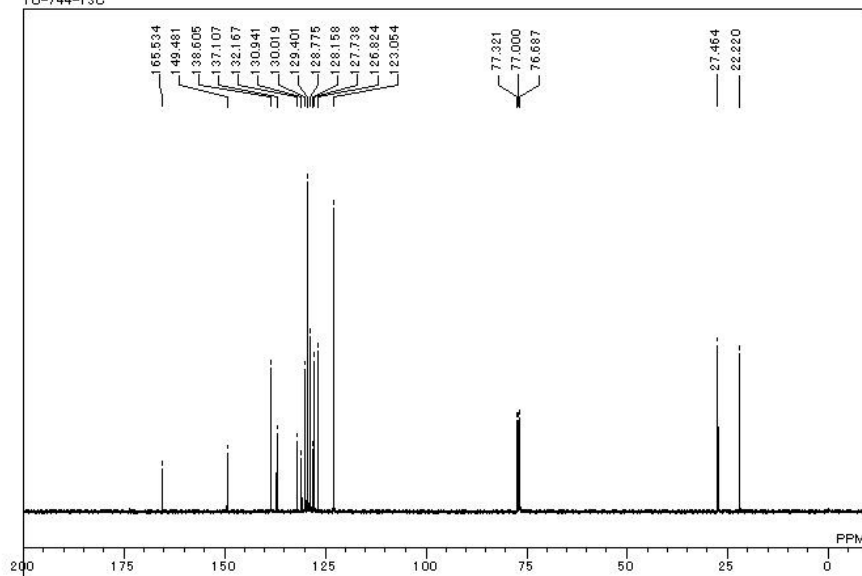
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TU-744



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EXMOD NON  
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OBSET 124.00 KHz  
OBFIN 10500.00 Hz  
POINT 16384  
FREQU 7992.01 Hz  
SCANS 8  
AQTM 2.0500 sec  
PD 4.9500 sec  
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CTEMP 22.0 c  
SLVNT CDCL3  
EXREF 0.00 ppm  
BF 0.12 Hz  
RGAIN 10

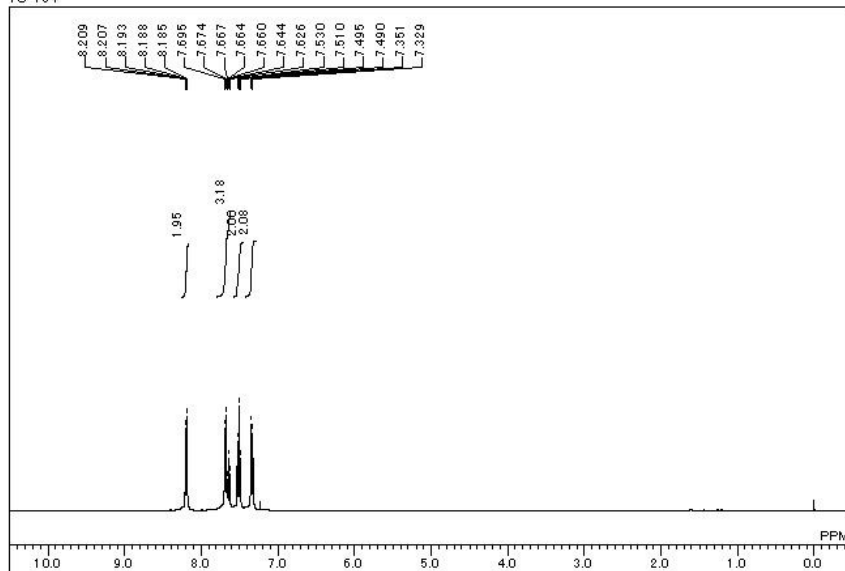


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TU-744-13C

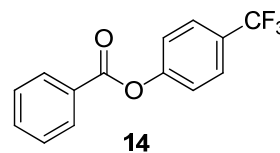


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OBSET 125.00 KHz  
OBFIN 10500.00 Hz  
POINT 32768  
FREQU 27118.64 Hz  
SCANS 256  
AQTM 1.2083 sec  
PD 1.7920 sec  
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IRNUC 1H  
CTEMP 22.8 c  
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BF 1.20 Hz  
RGAIN 26

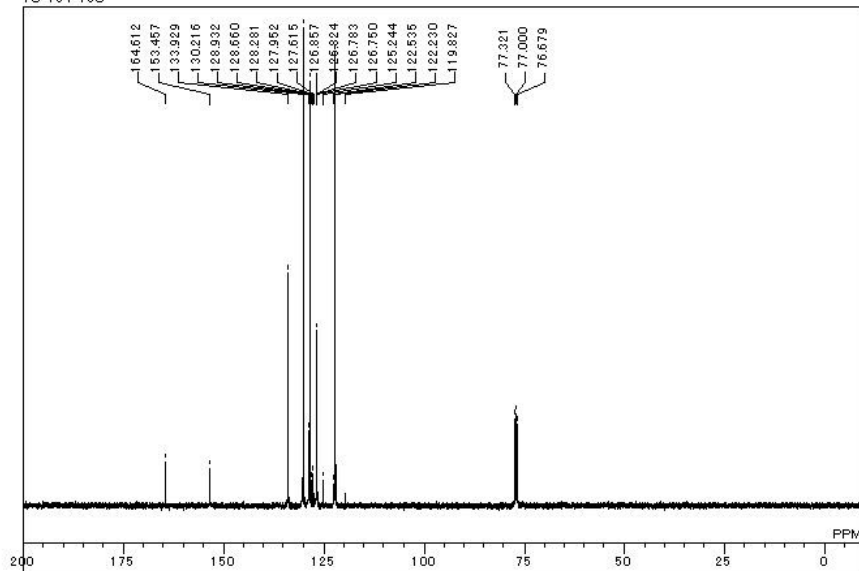
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TU-764



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EXMOD NON  
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OBFIN 10500.00 Hz  
POINT 16384  
FREQU 7992.01 Hz  
SCANS 8  
AQTM 2.0500 sec  
PD 4.9500 sec  
PWI 6.20 usec  
IRNUC 1H  
CTEMP 21.9 c  
SLVNT CDCL3  
EXREF 0.00 ppm  
BF 0.12 Hz  
RGAIN 9

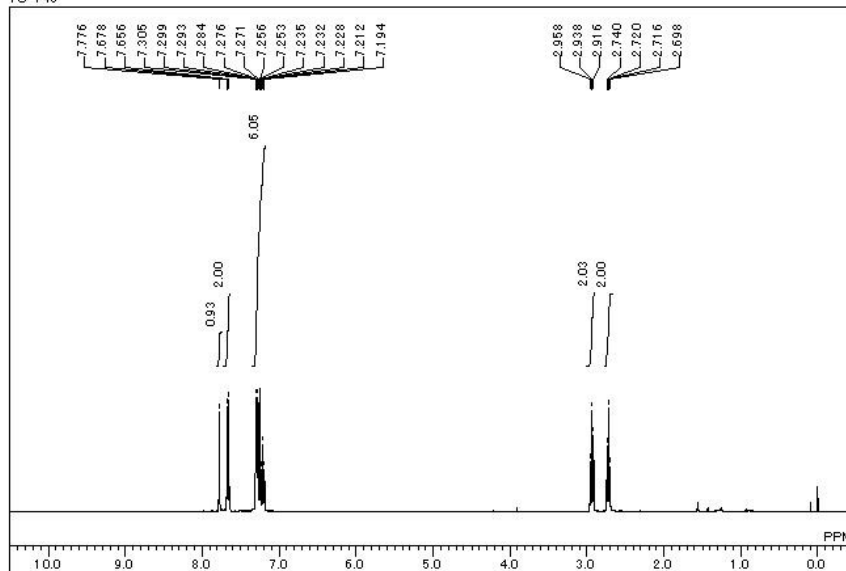


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TU-764-13C

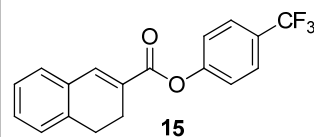


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OBSET 125.00 KHz  
OBFIN 10500.00 Hz  
POINT 32768  
FREQU 27118.64 Hz  
SCANS 128  
AQTM 1.2083 sec  
PD 1.7920 sec  
PWI 5.50 usec  
IRNUC 1H  
CTEMP 22.9 c  
SLVNT CDCL3  
EXREF 77.00 ppm  
BF 1.20 Hz  
RGAIN 26

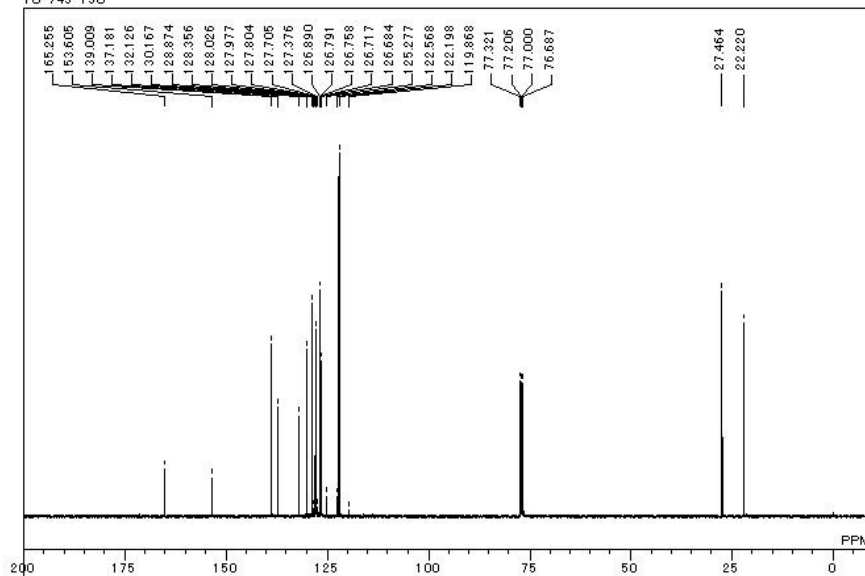
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TU-745



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QBNUC 1H  
EXMOD NON  
OBFRO 399.65 MHz  
OBSEI 124.00 KHz  
OBFIN 10500.00 Hz  
POINT 16384  
FREQU 7992.01 Hz  
SCANS 8  
AQTM 2.0500 sec  
PD 4.9500 sec  
PWI 6.20 usec  
IRNUC 1H  
CTEMP 22.8 c  
SLVNT CDCL3  
EXREF 0.00 ppm  
BF 0.12 Hz  
RGAIN 10

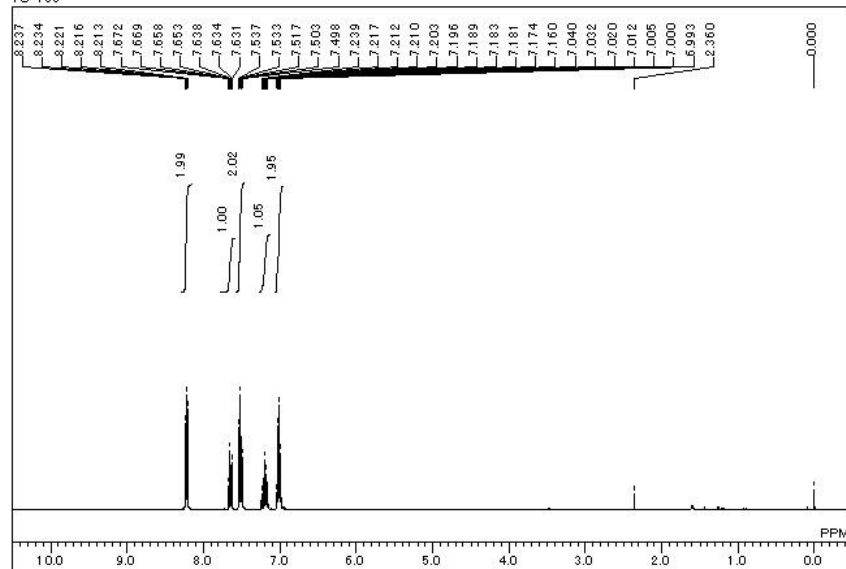


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TU-745-13C

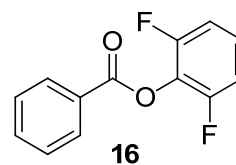


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OBSEI 125.00 KHz  
OBFIN 10500.00 Hz  
POINT 32768  
FREQU 27118.64 Hz  
SCANS 512  
AQTM 1.2083 sec  
PD 1.7920 sec  
PWI 5.50 usec  
IRNUC 1H  
CTEMP 23.0 c  
SLVNT CDCL3  
EXREF 77.00 ppm  
BF 1.20 Hz  
RGAIN 26

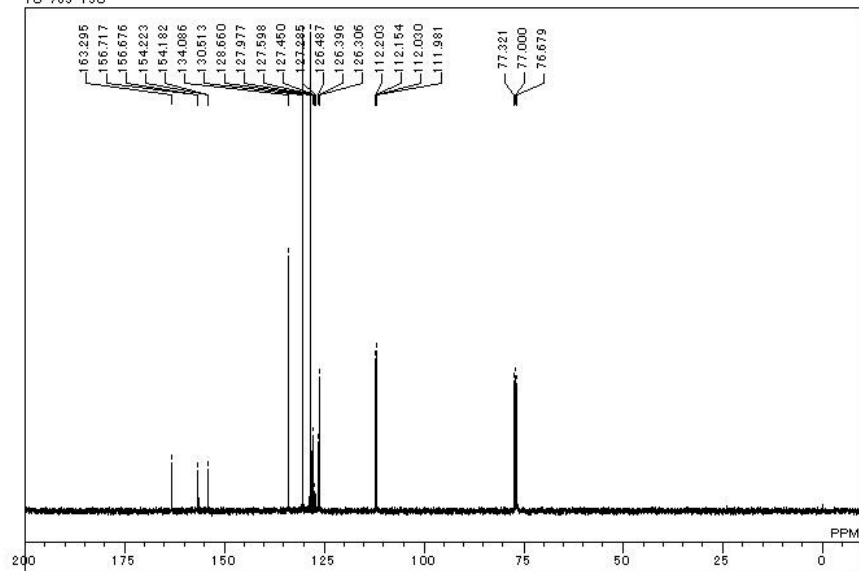
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TU-765



DFILE F:\JADS-Carbonylation NMR\TU-  
TU-765  
DATIM Mon Jun 18 19:35:15 2012  
OBNUC 1H  
EXMOD NON  
OBFREQ 399.65 MHz  
OBSET 124.00 KHz  
OBFIN 10500.00 Hz  
POINT 16384  
FREQU 7992.01 Hz  
SCANS 8  
AQTM 2.0500 sec  
PD 4.9500 sec  
PWI 6.20 usec  
IRNUC 1H  
CTEMP 22.1 c  
SLVNT CDCL3  
EXREF 0.00 ppm  
BF 0.12 Hz  
RGAIN 10



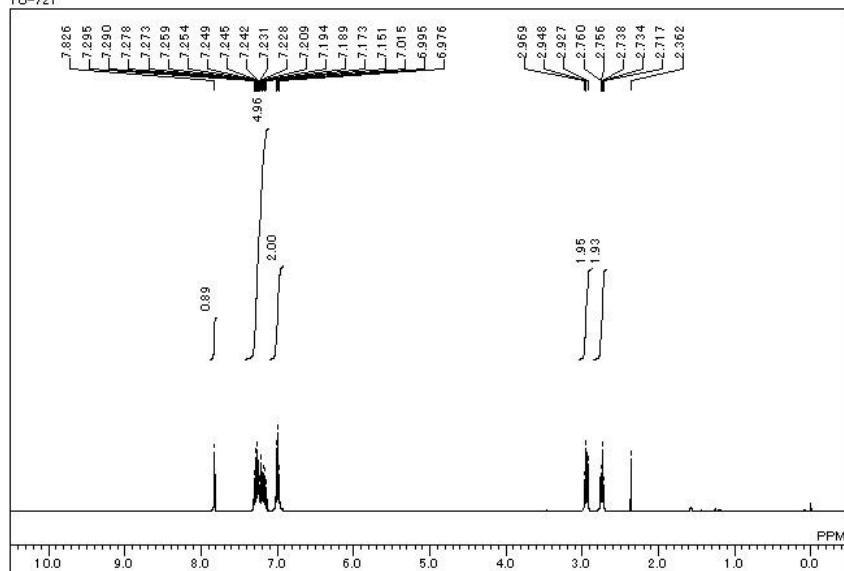
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TU-765-13C



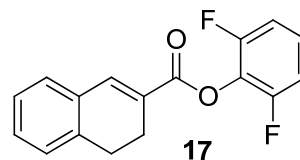
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DATIM Mon Jun 18 20:20:53 2012  
OBNUC 13C  
EXMOD BCM  
OBFREQ 100.40 MHz  
OBSET 125.00 KHz  
OBFIN 10500.00 Hz  
POINT 32768  
FREQU 27118.64 Hz  
SCANS 128  
AQTM 1.2083 sec  
PD 1.7920 sec  
PWI 5.50 usec  
IRNUC 13C  
CTEMP 23.1 c  
SLVNT CDCL3  
EXREF 77.00 ppm  
BF 1.20 Hz  
RGAIN 26



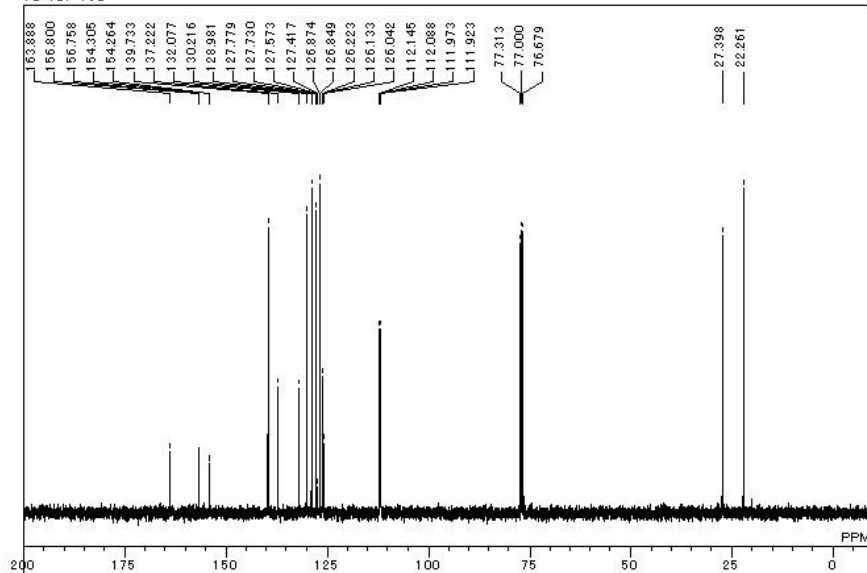
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TU-721



DFILE F:\Carbonylation(TL)\NMR\TU-721  
COMNT TU-721  
DATIM Wed May 30 11:33:12 2012  
OBNUC 1H  
EXMOD NON  
OBFRQ 399.65 MHz  
OBSET 124.00 KHz  
OBFIN 10500.00 Hz  
POINT 16384  
FREQU 7992.01 Hz  
SCANS 8  
ACQTM 2.0500 sec  
PD 4.9500 sec  
PWI 6.20 usec  
IRNUC 1H  
OTEMP 24.5 c  
SLVNT CDCL3  
EXREF 0.00 ppm  
BF 0.12 Hz  
RGAIN 11



F:\Carbonylation(TL)\NMR\TU-721-13C1\BOMJE3\_FT.als  
TU-721-13C



DFILE F:\Carbonylation(TL)\NMR\TU-721  
COMNT TU-721-13C  
DATIM Wed May 30 11:51:44 2012  
OBNUC 13C  
EXMOD BOM  
OBFRQ 100.40 MHz  
OBSET 125.00 KHz  
OBFIN 10500.00 Hz  
POINT 32768  
FREQU 27118.64 Hz  
SCANS 128  
ACQTM 1.2083 sec  
PD 1.7920 sec  
PWI 5.50 usec  
IRNUC 1H  
OTEMP 24.5 c  
SLVNT CDCL3  
EXREF 77.00 ppm  
BF 1.20 Hz  
RGAIN 28