

Supporting Information

Nickel-catalyzed cross-coupling of carboxylic anhydrides with arylboronic acids

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General remarks

All reactions were carried out under nitrogen atmosphere with oven-dried glassware. *Trans*-chloro(1-naphthyl)bis(triphenylphosphine)nickel(II) was prepared according to the published procedures.¹ Toluene, THF and dioxane were distilled from sodium/benzophenone before use. Potassium carbonate, potassium phosphate, sodium carbonate were commercially available and used with finely-ground powder. All ligands were purchased commercially and used as received. Carboxylic anhydrides were commercially supplied and used without further purification. Column chromatography was performed on silica gel (200–300 mesh). All yields were referred to isolated yields (average of two runs) of compounds estimated to be >95% pure as determined by ¹H NMR. All the products are known compounds and partly characterized by melting points (for solid samples), MS, ¹H and ¹³C NMR, and compared to authentic samples or the literature data. Melting points were measured with a X-4 micro melting point apparatus and uncorrected.

Synthesis of Ni(PPh₃)₂(1-naphthyl)Cl (C-1). A stirred mixture of NiCl₂·6H₂O (4.8 g, 0.02 mol), triphenylphosphane (11.53 g, 0.044 mol) and 95% ethanol (90 mL) was heated until a gentle reflux started. 1-Chloronaphthalene (6.5 g, 0.04 mol, excess) was then added, followed by zinc dust (1.3 g, 0.02 mol) over 5 min. The dark-green mixture very soon turned yellow. After stirring and heating under reflux for 1.5 h (under nitrogen), the mixture was cooled to room temperature. Four 2-mL portions of 30% aqueous hydrochloric acid were added over 15 min. After stirring for 1.5 h, the solid was filtered off on a sintered-glass funnel and successively washed with 20 mL of ethanol, twice with 20 mL of 1 M aqueous hydrochloric acid, twice with 20 mL of ethanol and once with 20 mL of petroleum (30–60 °C). The yellow solid was dried in vacuo at a bath temperature of not higher than 45°C. The yield was above 80%.

General procedure for the nickel-catalyzed cross-couplings of carboxylic anhydrides with arylboronic acids

An oven-dried 25-mL three-necked flask was charged with K₃PO₄ (3.0 mmol), Ni(PPh₃)₂(1-naphthyl)Cl (0.05 mmol) and PCy₃ (0.1 mmol). Then the carboxylic anhydrides (1.0 mmol) (if solid) and the arylboronic acid (1.5 mmol) were added. The

flask was evacuated and backfilled with nitrogen, with the operation being repeated twice. The carboxylic anhydrides (if liquid), dried toluene (5.0 mL) were added via syringe at this time. The reaction mixture was heated in an oil bath of 50 °C for 12 h and then allowed to cool to room temperature; it was then filtered through a silica-gel pad that was washed with ethyl acetate. The combined organic phases were evaporated under reduced pressure and the residue purified by silica-gel column chromatography to give the desired product.

Characterization data of the products

(4-Methoxyphenyl)phenylmethanone (Table 2, entries 1 and 13). Colorless solid: mp 59–60 °C (lit.² mp 60–62 °C). ¹H NMR (CDCl₃, 400 MHz): δ 7.83 (d, *J* = 8.8 Hz, 2H), 7.75 (d, *J* = 7.2 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 6.96 (d, *J* = 8.8 Hz, 2H), 3.89 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz): δ 195.6, 163.3, 138.4, 132.6, 132.0, 130.2, 129.8, 128.3, 113.6, 55.6; MS (EI, *m/z*, rel.%): 212 (M⁺, 30%), 135 ([M-77]⁺, 100%). CAS Number: 611-94-9.

(3-Methoxyphenyl)phenylmethanone (Table 2, entry 2). Colorless solid: mp 35–36 °C (lit.³ mp 37 °C). ¹H NMR (CDCl₃, 400 MHz): δ 7.81 (d, *J* = 7.6 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.41–7.32 (m, 3H), 7.13 (d, *J* = 7.6 Hz, 1H), 3.86 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz): δ 196.6, 159.6, 138.9, 137.7, 132.5, 130.1, 129.3, 128.3, 122.9, 118.9, 114.4, 55.5; MS (EI, *m/z*, rel.%): 212 (M⁺, 100%), 135 ([M-77]⁺, 90%), 105 ([M-107]⁺, 60%), 77 ([M-135]⁺, 25%). CAS Number: 6136-67-0.

Phenyl(*p*-tolyl)methanone (Table 2, entry 3). Colorless solid: mp 55–56 °C (lit.² mp 57–58 °C). ¹H NMR (CDCl₃, 400 MHz): δ 7.78 (d, *J* = 7.2 Hz, 2H), 7.72 (d, *J* = 8.4 Hz, 2H), 7.57 (t, *J* = 7.2 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 2.44 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz): δ 196.4, 143.2, 137.9, 134.9, 132.2, 130.3, 129.9, 129.0, 128.2, 21.6; MS (EI, *m/z*, rel.%): 196 (M⁺, 50%), 149 ([M-47]⁺, 30%), 119 ([M-77]⁺, 100%). CAS Number: 134-84-9.

Phenyl(*m*-tolyl)methanone (Table 2, entry 4). Colorless oil. ¹H NMR (CDCl₃, 400 MHz): δ 7.80 (d, *J* = 7.6 Hz, 2H), 7.63 (s, 1H), 7.61–7.56 (m, 2H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.42–7.34 (m, 2H), 2.42 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz): δ 196.9,

138.1, 137.7, 137.6, 133.2, 132.3, 130.4, 130.0, 128.2, 128.1, 127.3, 21.3; MS (EI, *m/z*, rel.%): 196 (M^+ , 75%), 119 ($[M-77]^+$, 100%), 105 ($[M-91]^+$, 60%), 77 ($[M-119]^+$, 20%). CAS Number: 643-65-2.

Benzophenone (Table 2, entry 5). Colorless solid: mp 47–48 °C (lit.² mp 48–49 °C). ¹H NMR (CDCl₃, 400 MHz): δ 7.81 (d, *J* = 7.6 Hz, 4H), 7.59 (t, *J* = 7.4 Hz, 6H), 7.48 (t, *J* = 7.6 Hz, 6H); ¹³C NMR (CDCl₃, 100 MHz): δ 196.8, 137.7, 132.5, 130.1, 128.4; MS (EI, *m/z*, rel.%): 182 (M^+ , 50%), 105 ($[M-77]^+$, 100%), 77 ($[M-105]^+$, 20%). CAS Number: 119-61-9.

(1-Naphthyl)phenylmethanone (Table 2, entry 6). Colorless solid: mp 74–75 °C (lit.² mp 76–77 °C). ¹H NMR (CDCl₃, 400 MHz): δ 8.10 (d, *J* = 8.4 Hz, 1H), 8.01 (d, *J* = 8.0 Hz, 1H), 7.93 (d, *J* = 7.6 Hz, 1H), 7.87 (d, *J* = 7.6 Hz, 2H), 7.60 (q, *J* = 8.1 Hz, 2H), 7.53 (t, *J* = 7.2 Hz, 3H), 7.47 (t, *J* = 7.6 Hz, 2H); ¹³C NMR (CDCl₃, 100 MHz): δ 197.9, 138.3, 136.3, 133.7, 133.2, 131.2, 130.9, 130.3, 128.4, 127.7, 127.2, 126.4, 125.6, 124.3; MS (EI, *m/z*, rel.%): 232 (M^+ , 100%), 155 ($[M-77]^+$, 95%), 127 ($[M-105]^+$, 60%), 105 ($[M-127]^+$, 50%), 77 ($[M-155]^+$, 25%). CAS Number: 642-29-5.

(4-Fluorophenyl)phenylmethanone (Table 2, entries 8 and 19). Colorless solid: mp 44–45 °C (lit.⁴ mp 47–49 °C). ¹H NMR (CDCl₃, 400 MHz): δ 7.85 (dd, *J* = 8.8, 5.6 Hz, 2H), 7.77 (d, *J* = 7.6 Hz, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.16 (t, *J* = 8.6 Hz, 2H); ¹³C NMR (CDCl₃, 100 MHz): δ 195.3, 165.4 (d, *J* = 252 Hz), 137.5, 133.9, 132.7 (d, *J* = 9.1 Hz), 132.5, 129.9, 128.4, 115.5 (d, *J* = 21.7 Hz); MS (EI, *m/z*, rel.%): 200 (M^+ , 95%), 123 ($[M-77]^+$, 100%), 105 ($[M-95]^+$, 50%), 77 ($[M-123]^+$, 15%). CAS Number: 345-83-5.

Bis(4-methoxyphenyl)methanone (Table 2, entry 9). Colorless solid: mp 134–135 °C (lit.⁵ mp 135–137 °C). ¹H NMR (CDCl₃, 400 MHz): δ 7.79 (d, *J* = 8.4 Hz, 4H), 6.96 (d, *J* = 8.4 Hz, 4H), 3.89 (s, 6H); ¹³C NMR (CDCl₃, 100 MHz): δ 194.3, 162.8, 132.1, 130.6, 113.4, 55.4; MS (EI, *m/z*, rel.%): 242 (M^+ , 30%), 135 ($[M-107]^+$, 100%). CAS Number: 90-96-0.

(3-Methoxyphenyl)(4-methoxyphenyl)methanone (Table 2, entry 10). Colorless oil. ¹H NMR (CDCl₃, 400 MHz): δ 7.83 (d, *J* = 8.8 Hz, 2H), 7.37 (t, *J* = 8.0 Hz, 1H), 7.30 (s, 2H), 7.11 (d, *J* = 7.2 Hz, 1H), 6.96 (d, *J* = 8.4 Hz, 2H), 3.89 (s, 3H),

3.85 (s, 3H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 195.0, 163.1, 159.3, 139.4, 132.4, 129.9, 129.0, 122.2, 118.0, 114.1, 113.4, 55.3, 55.2; MS (EI, m/z , rel.%): 242 (M^+ , 15%), 135 ($[\text{M}-107]^+$, 100%). CAS Number: 75731-44-1.

(4-Methoxyphenyl)(*p*-tolyl)methanone (Table 2, entry 11). Colorless solid: mp 85–86 $^{\circ}\text{C}$ (lit.² mp 87–89 $^{\circ}\text{C}$). ^1H NMR (CDCl_3 , 400 MHz): δ 7.81 (d, J = 8.8 Hz, 2H), 7.67 (d, J = 8.0 Hz, 2H), 7.28 (d, J = 8.0 Hz, 2H), 6.96 (d, J = 8.8 Hz, 2H), 3.88 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 195.4, 163.1, 142.7, 135.6, 132.5, 130.5, 130.1, 128.9, 113.5, 55.5, 21.7; MS (EI, m/z , rel.%): 226 (M^+ , 40%), 135 ($[\text{M}-91]^+$, 100%), 119 ($[\text{M}-107]^+$, 20%). CAS Number: 23886-71-7.

(4-Methoxyphenyl)(*m*-tolyl)methanone (Table 2, entry 12). Colorless solid: mp 53–54 $^{\circ}\text{C}$ (lit.⁶ mp 56 $^{\circ}\text{C}$). ^1H NMR (CDCl_3 , 400 MHz): δ 7.82 (d, J = 8.8 Hz, 2H), 7.57 (s, 1H), 7.52 (d, J = 6.8 Hz, 1H), 7.40–7.32 (m, 2H), 6.96 (d, J = 8.8 Hz, 2H), 3.89 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 195.6, 163.1, 138.2, 137.9, 132.5, 132.4, 130.1, 130.0, 127.9, 126.9, 113.4, 55.3, 21.2; MS (EI, m/z , rel.%): 226 (M^+ , 30%), 135 ($[\text{M}-91]^+$, 100%). CAS Number: 53039-63-7.

(4-Methoxyphenyl)(1-naphthyl)methanone (Table 2, entry 14). Colorless solid: mp 79–80 $^{\circ}\text{C}$ (lit.⁷ mp 81–82 $^{\circ}\text{C}$). ^1H NMR (CDCl_3 , 400 MHz): δ 8.00 (t, J = 6.8 Hz, 2H), 7.91 (d, J = 7.6 Hz, 1H), 7.85 (d, J = 9.2 Hz, 2H), 7.58–7.45 (m, 4H), 6.93 (d, J = 8.8 Hz, 2H), 3.87 (s, 3H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 196.7, 163.8, 137.0, 133.6, 132.7, 131.0, 130.8, 130.6, 128.3, 127.0, 126.8, 126.3, 125.7, 124.4, 113.7, 55.5; MS (EI, m/z , rel.%): 262 (M^+ , 50%), 135 ($[\text{M}-127]^+$, 100%). CAS Number: 39070-92-3.

(4-Fluorophenyl)(4-methoxyphenyl)methanone (Table 2, entries 16 and 17). Colorless solid: mp 94–95 $^{\circ}\text{C}$ (lit.⁸ mp 96 $^{\circ}\text{C}$). ^1H NMR (CDCl_3 , 400 MHz): δ 7.79 (dt, J = 8.8 Hz, 2.6 Hz, 4H), 7.15 (t, J = 8.6 Hz, 2H), 6.97 (d, J = 8.8 Hz, 2H), 3.89 (s, 3H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 194.2, 165.2 (d, J = 252 Hz), 163.4, 134.5, 132.5, 132.4 (d, J = 9.0 Hz), 130.1, 115.4 (d, J = 21.6 Hz), 113.7, 55.6; MS (EI, m/z , rel.%): 230 (M^+ , 40%), 135 ($[\text{M}-95]^+$, 100%). CAS Number: 345-89-1.

(4-Fluorophenyl)(*p*-tolyl)methanone (Table 2, entry 18). Colorless solid: mp 93–94 $^{\circ}\text{C}$ (lit.⁹ mp 95–96 $^{\circ}\text{C}$). ^1H NMR (CDCl_3 , 400 MHz): δ 7.82 (dd, J = 8.4 Hz, 5.6

Hz, 2H), 7.69 (d, $J = 7.6$ Hz, 2H), 7.29 (d, $J = 8.0$ Hz, 2H), 7.15 (t, $J = 8.4$ Hz, 2H), 2.44 (s, 3H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 195.0, 165.3 (d, $J = 252$ Hz), 143.4, 134.8, 134.2, 132.5 (d, $J = 9.0$ Hz), 130.2, 129.1, 115.4 (d, $J = 21.7$ Hz), 21.7; MS (EI, m/z , rel.%): 214 (M^+ , 50%), 123 ($[\text{M}-91]^+$, 40%), 119 ($[\text{M}-95]^+$, 100%). CAS Number: 530-46-1.

Phenyl(thiophen-3-yl)methanone (Table 2, entry 22). Colorless solid: mp 61–62 $^{\circ}\text{C}$ (lit.¹⁰ mp 63 $^{\circ}\text{C}$). ^1H NMR (CDCl_3 , 400 MHz): δ 7.93 (dd, $J = 2.8$ Hz, 0.8 Hz, 1H), 7.85 (d, $J = 7.2$ Hz, 2H), 7.63–7.57 (m, 2H), 7.49 (t, $J = 7.6$ Hz, 2H), 7.38 (q, $J = 2.8$ Hz, 1H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 189.8, 141.2, 138.5, 133.9, 132.2, 129.3, 128.5, 128.3, 126.2; MS (EI, m/z , rel.%): 188 (M^+ , 100%), 111 ($[\text{M}-77]^+$, 95%), 105 ($[\text{M}-83]^+$, 25%). CAS Number: 6453-99-2.

(4-Methoxyphenyl)(thiophen-3-yl)methanone (Table 2, entry 23). Colorless solid: mp 60–62 $^{\circ}\text{C}$ (lit.¹¹ mp 61–65 $^{\circ}\text{C}$). ^1H NMR (CDCl_3 , 400 MHz): δ 7.89 (s, 1H), 7.88 (d, $J = 8.8$ Hz, 2H), 7.56 (dd, $J = 5.2$ Hz, 0.8 Hz, 1H), 7.37 (q, $J = 2.4$ Hz, 1H), 6.97 (d, $J = 8.8$ Hz, 2H), 3.89 (s, 3H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 188.6, 163.0, 141.3, 132.6, 131.7, 130.9, 128.5, 125.9, 113.5, 55.3; MS (EI, m/z , rel.%): 218 (M^+ , 70%), 135 ($[\text{M}-83]^+$, 100%), 111 ($[\text{M}-107]^+$, 30%). CAS Number: 5064-00-6.

(4-Fluorophenyl)(thiophen-3-yl)methanone (Table 2, entry 24). Colorless solid: mp 72–75 $^{\circ}\text{C}$. ^1H NMR (CDCl_3 , 400 MHz): δ 7.93–7.87 (m, 3H), 7.57 (dd, $J = 5.2$ Hz, 0.8 Hz, 1H), 7.40 (q, $J = 2.8$ Hz, 1H), 7.17 (t, $J = 8.6$ Hz, 2H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 188.5, 165.0 (d, $J = 252$ Hz), 141.1, 134.8, 133.7, 132.0 (d, $J = 9.0$ Hz), 128.6, 126.4, 115.6 (d, $J = 21.7$ Hz); MS (EI, m/z , rel.%): 206 (M^+ , 95%), 123 ($[\text{M}-83]^+$, 50%), 111 ($[\text{M}-95]^+$, 100%), 95 ($[\text{M}-111]^+$, 25%). CAS Number: 64844-96-8.

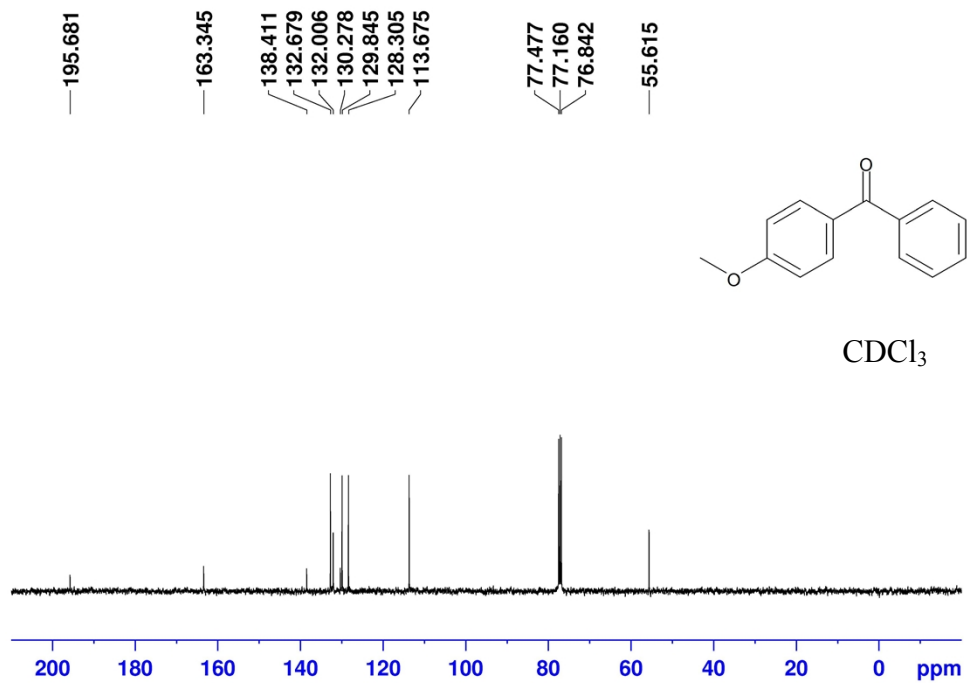
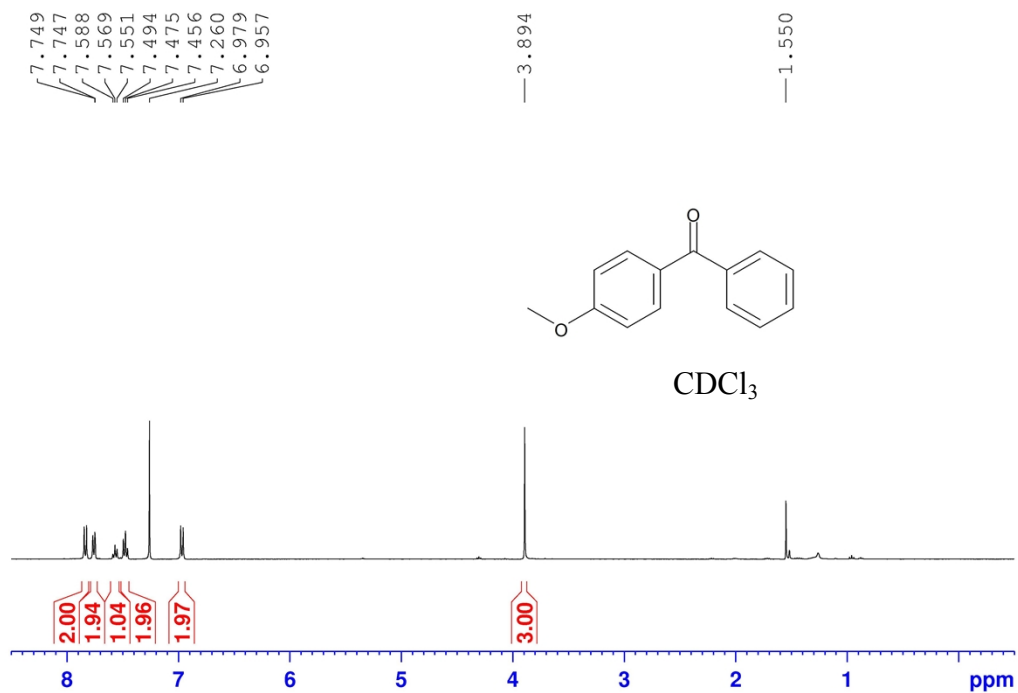
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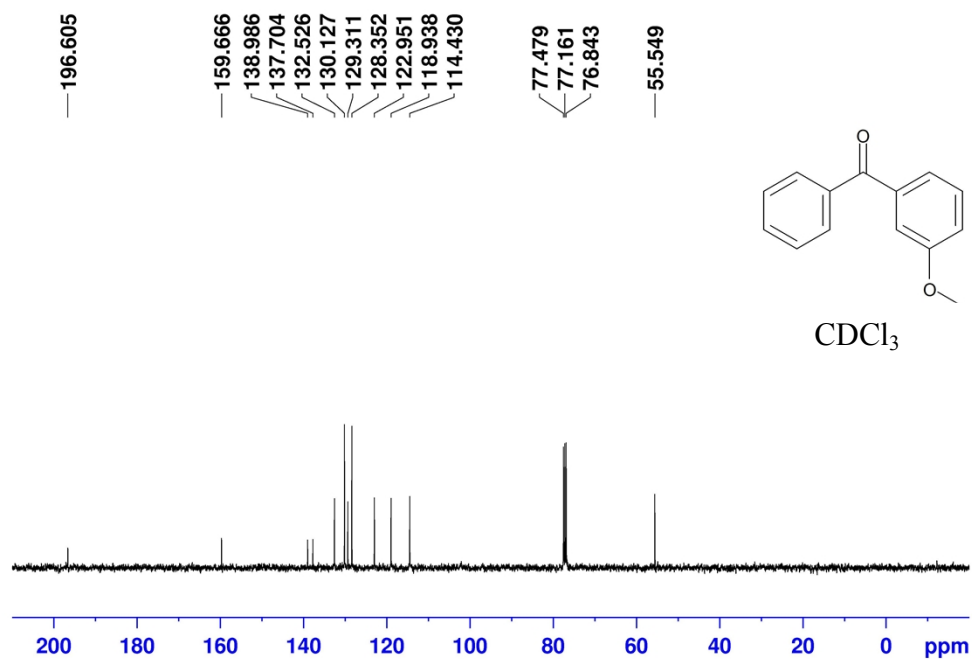
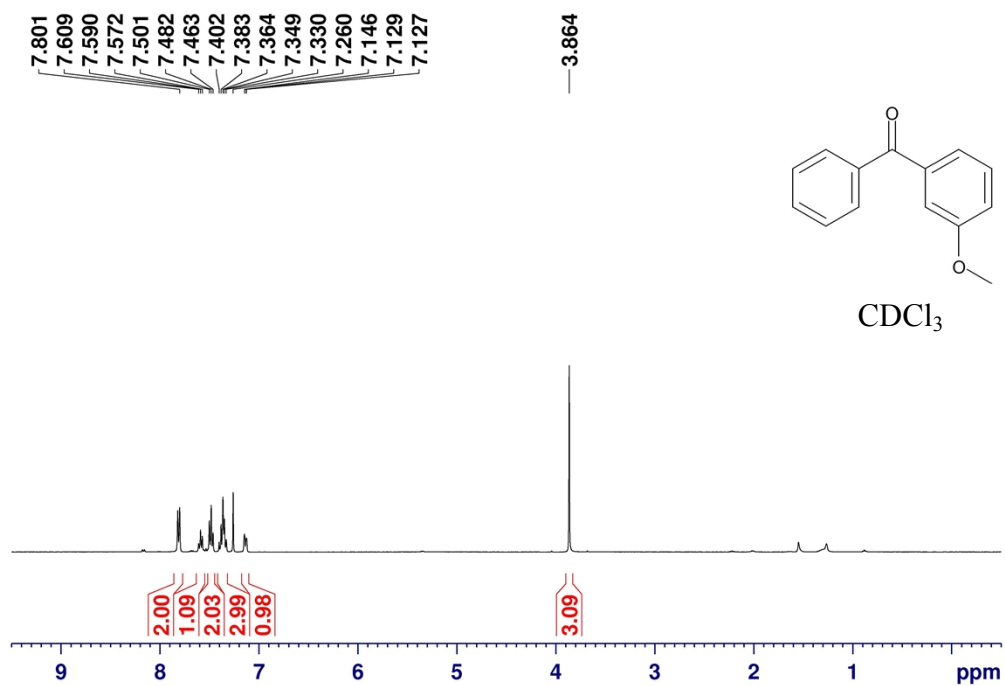
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¹H NMR and ¹³C NMR spectra of the products

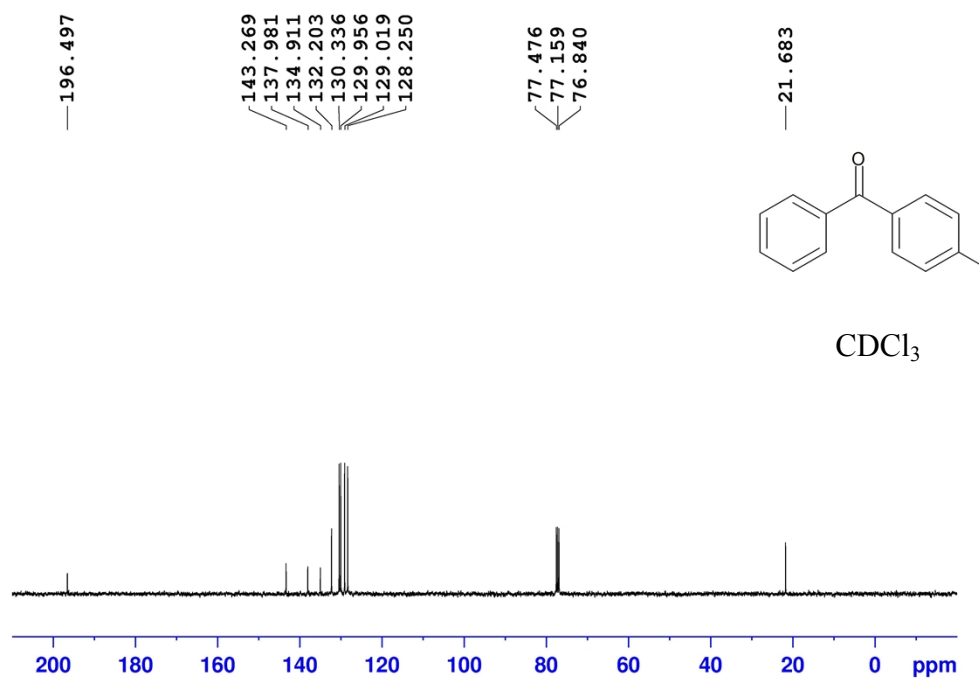
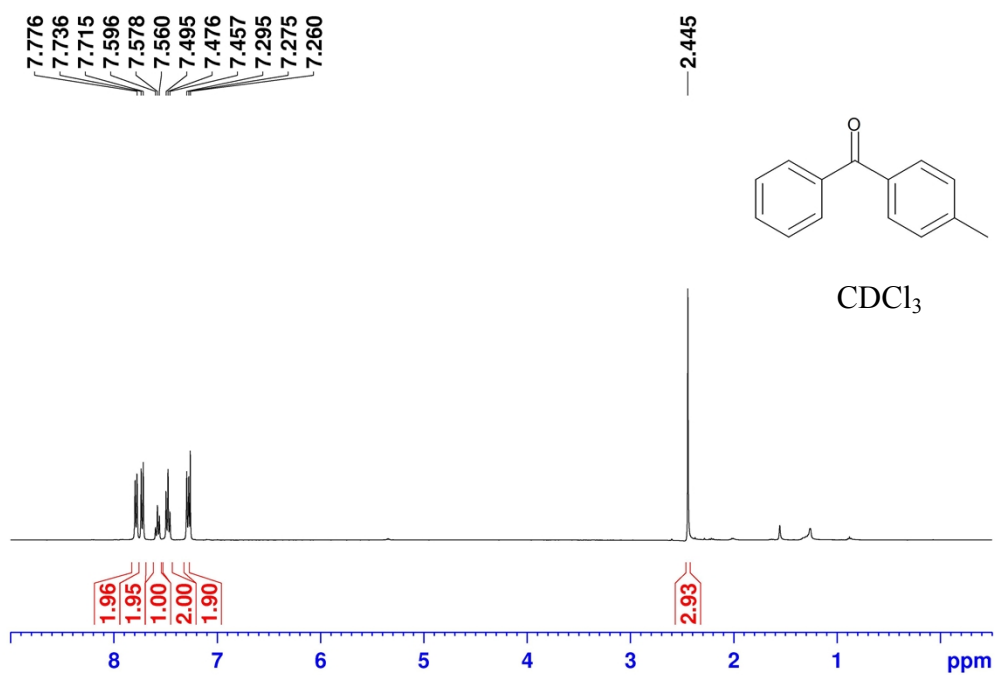
(4-Methoxyphenyl)(phenyl)methanone (Table 2, entries 1 and 13)



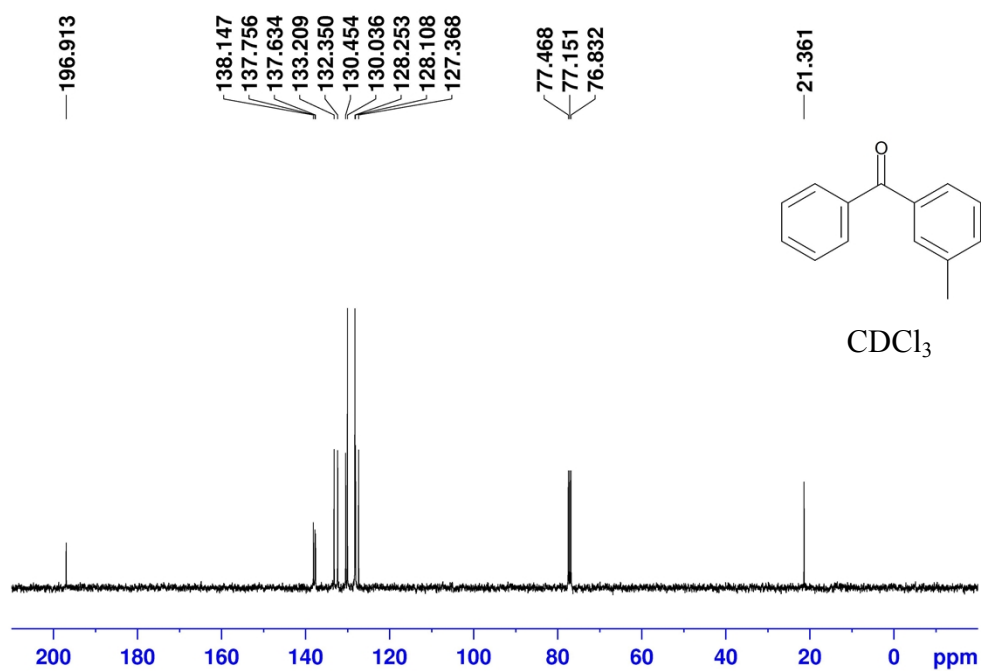
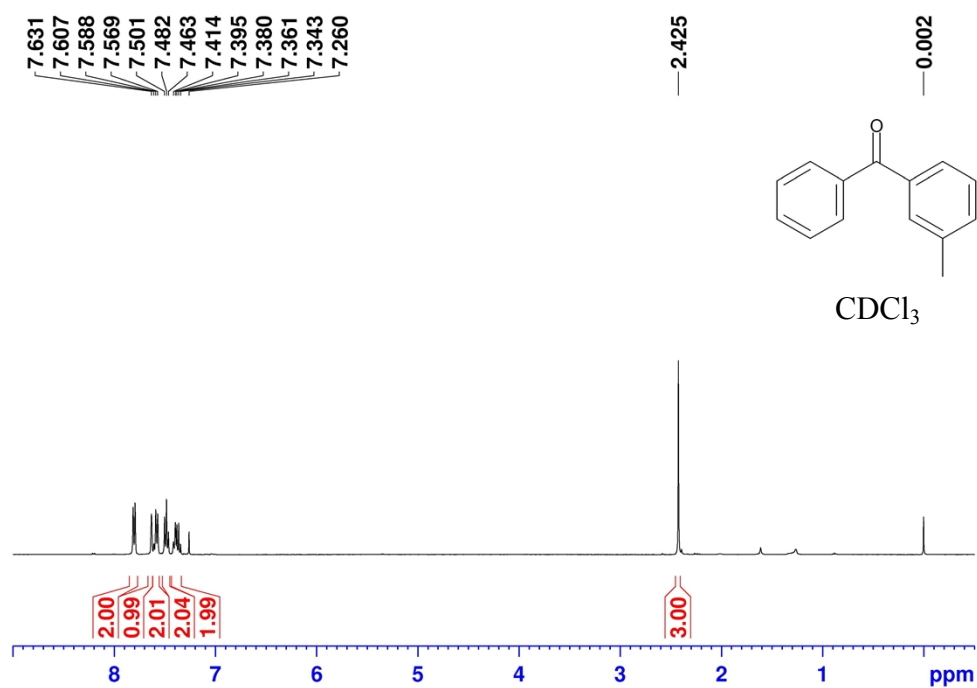
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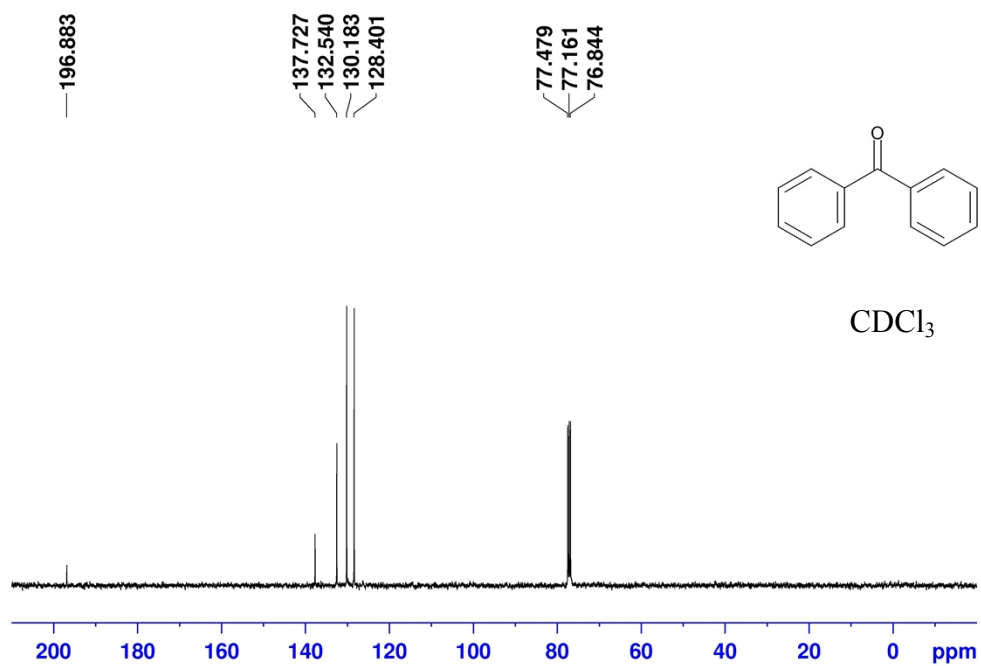
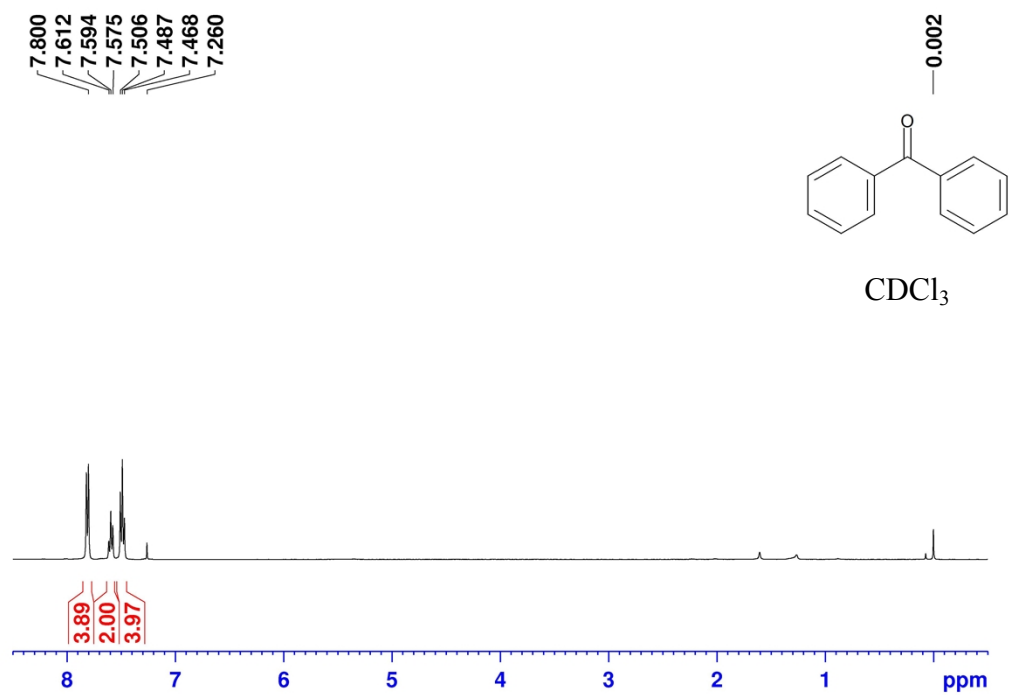
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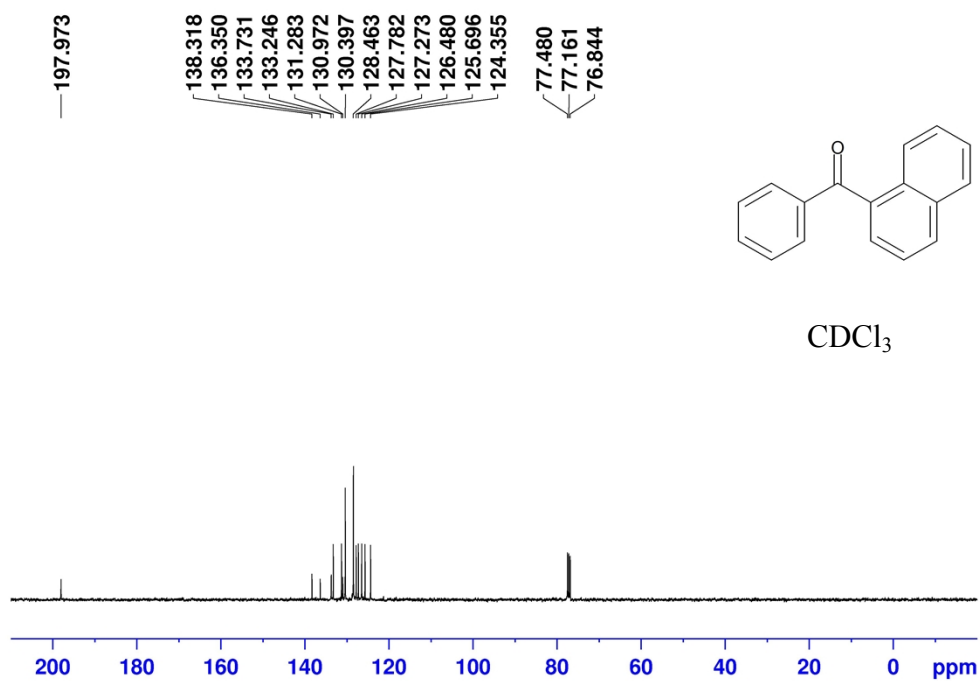
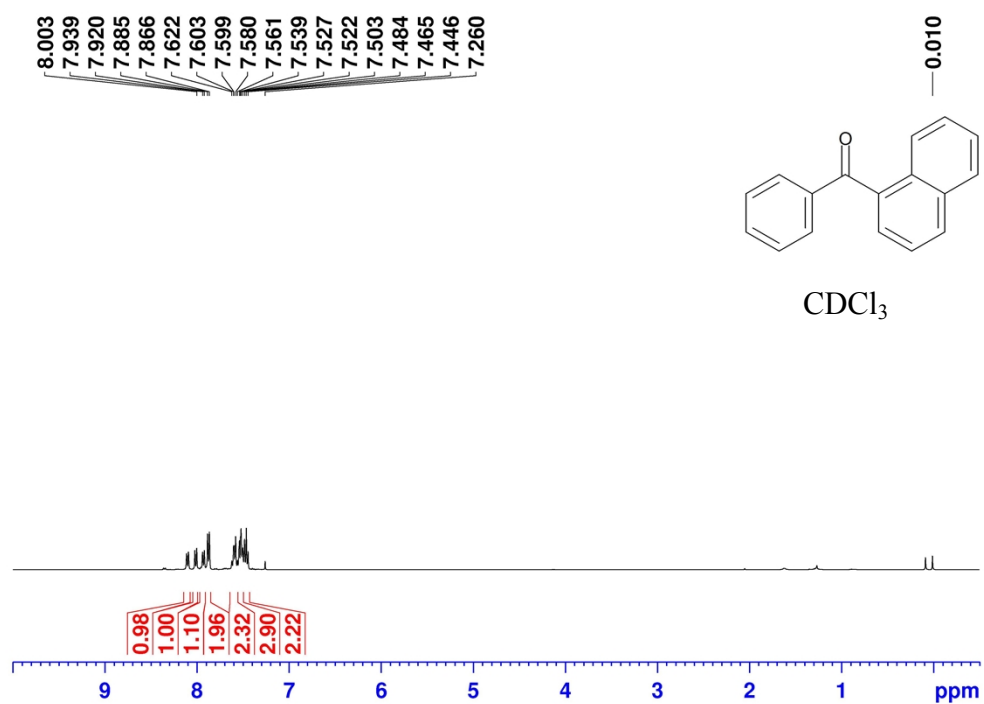
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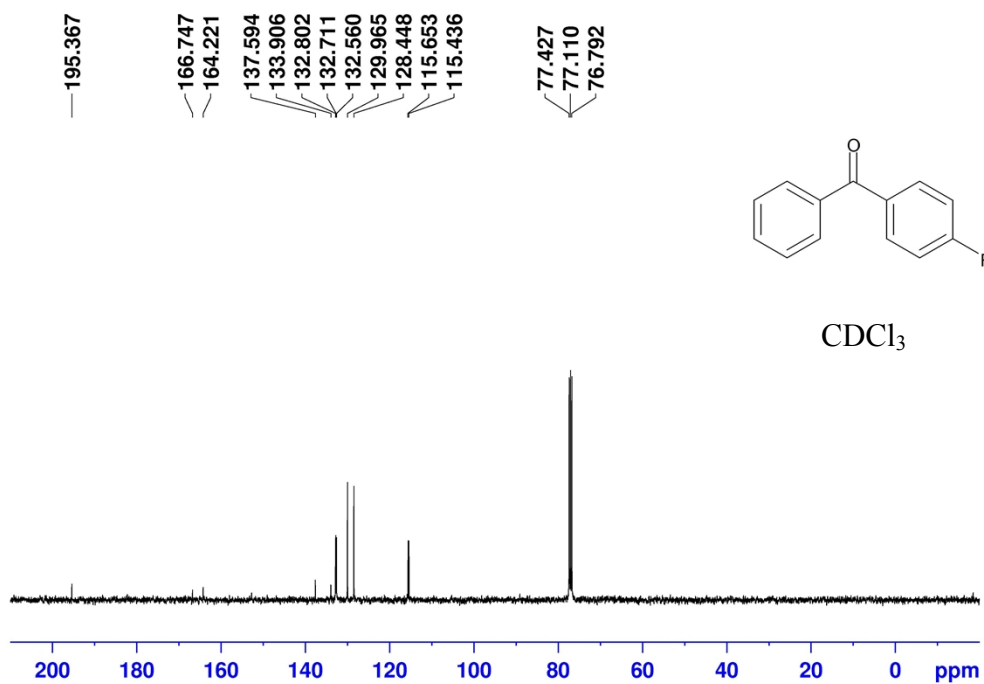
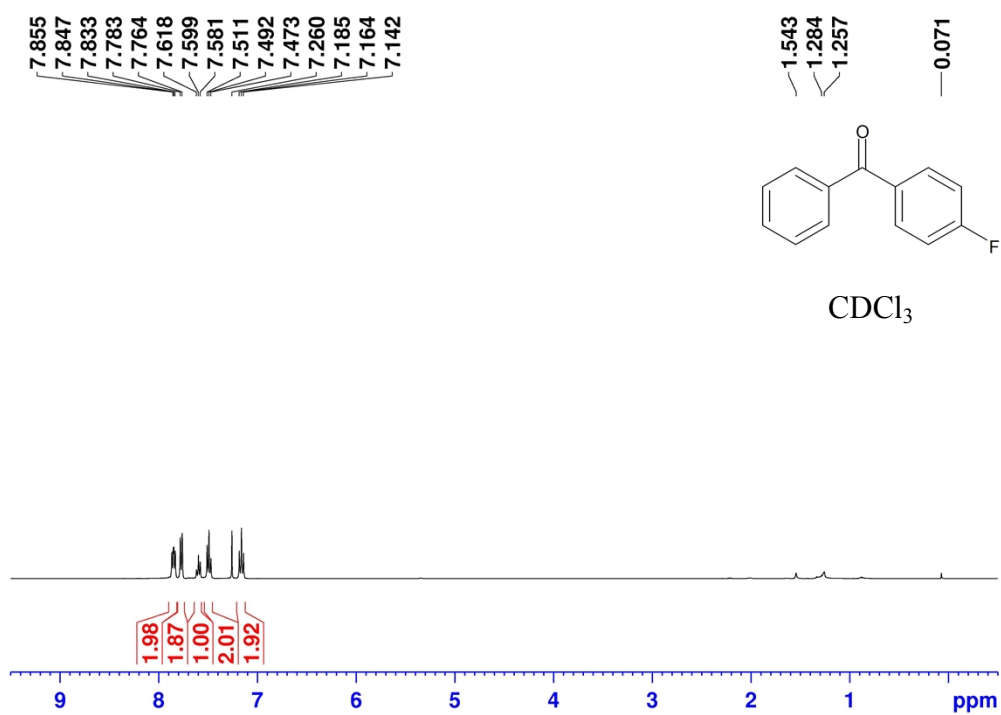
Benzophenone (Table 2, entry 5)



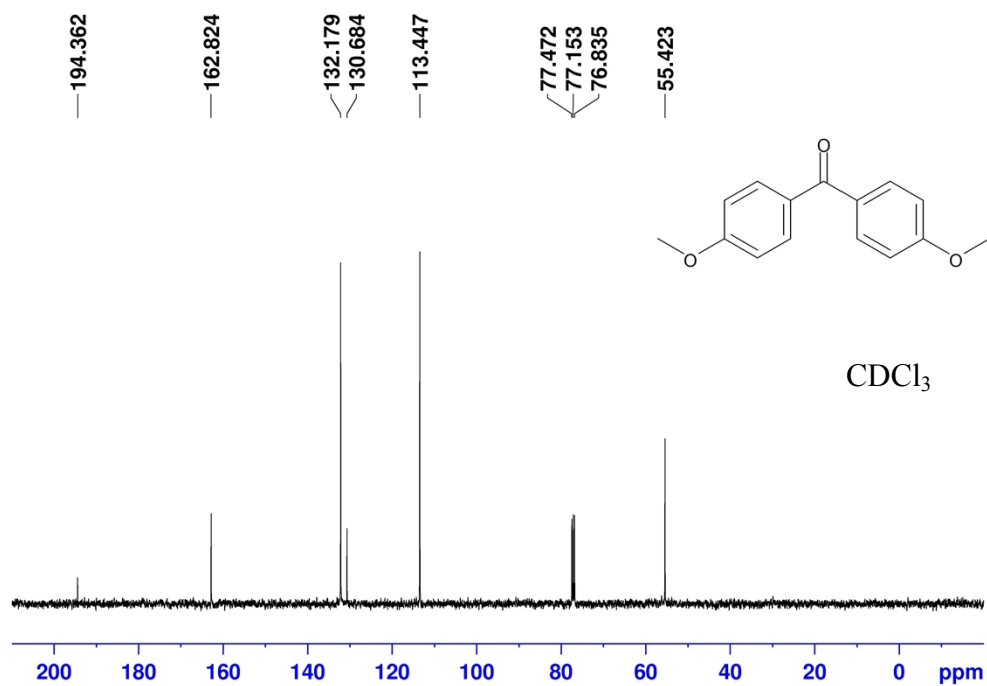
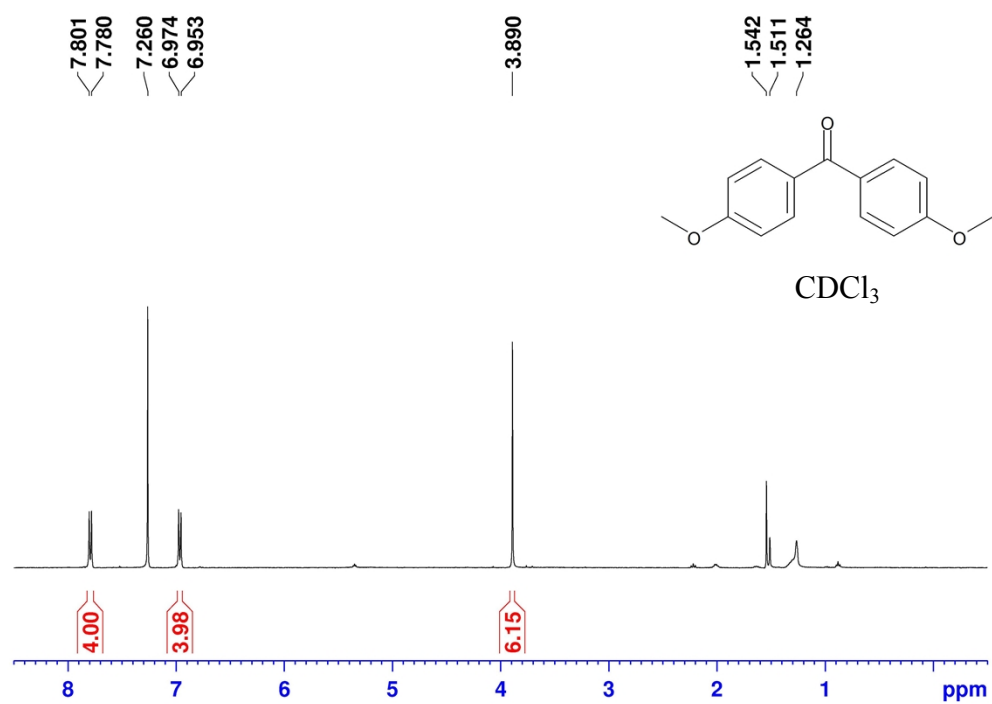
(1-Naphthyl)(phenyl)methanone (Table 2, entry 6)



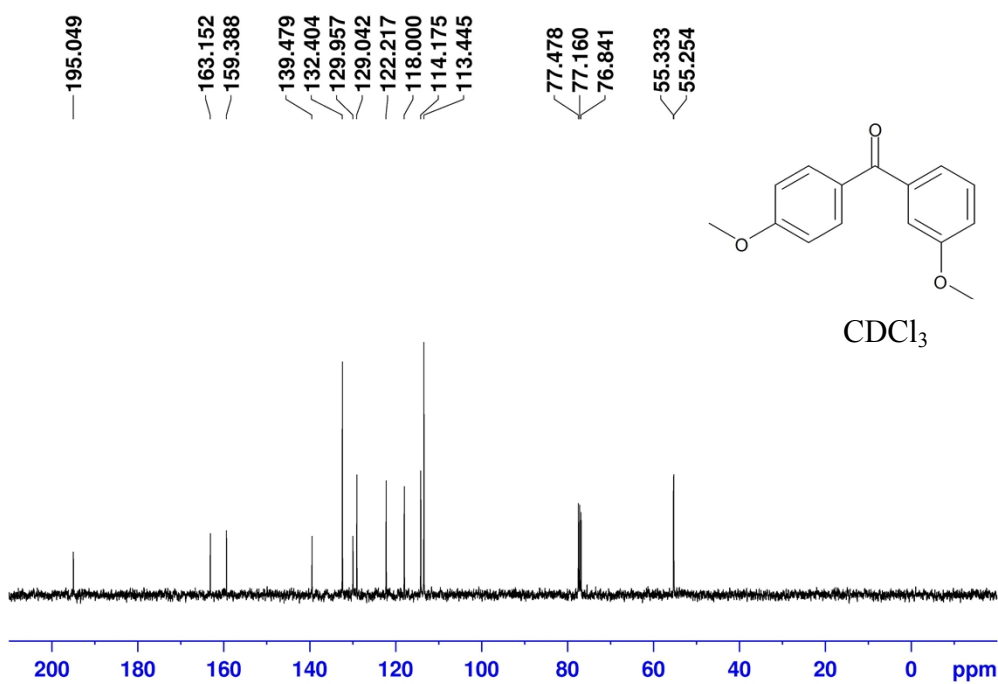
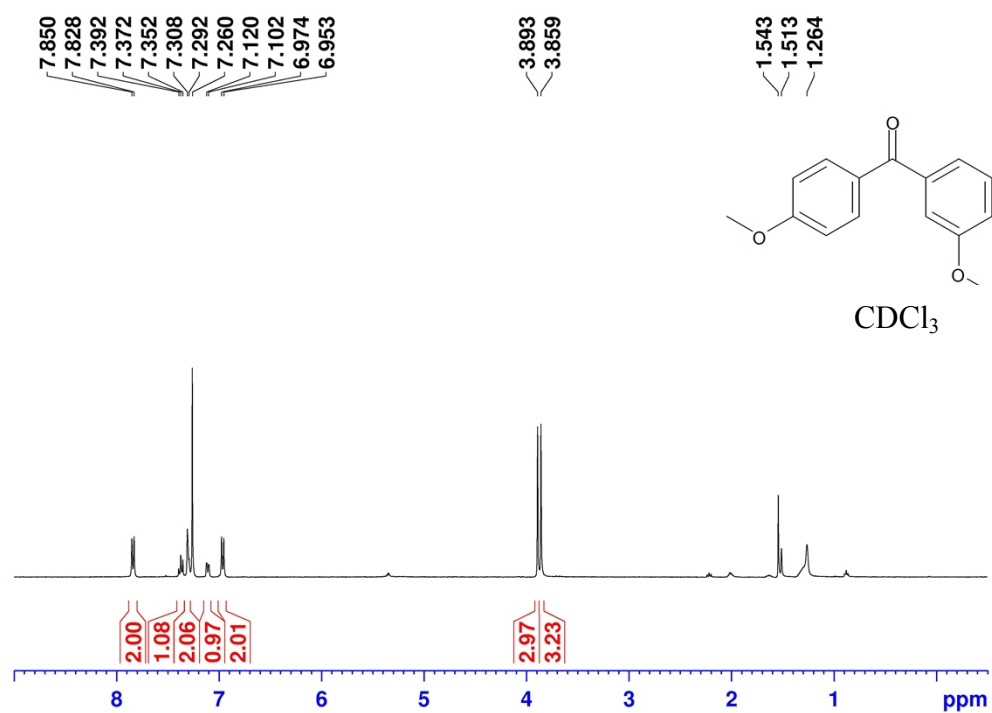
(4-Fluorophenyl)(phenyl)methanone (Table 2, entries 8 and 19)



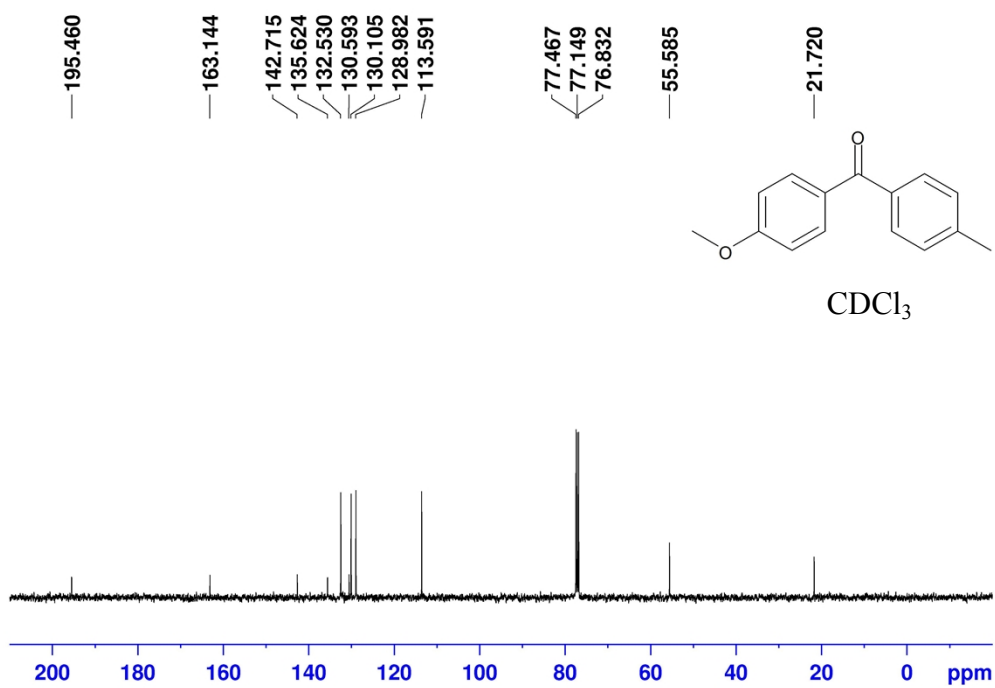
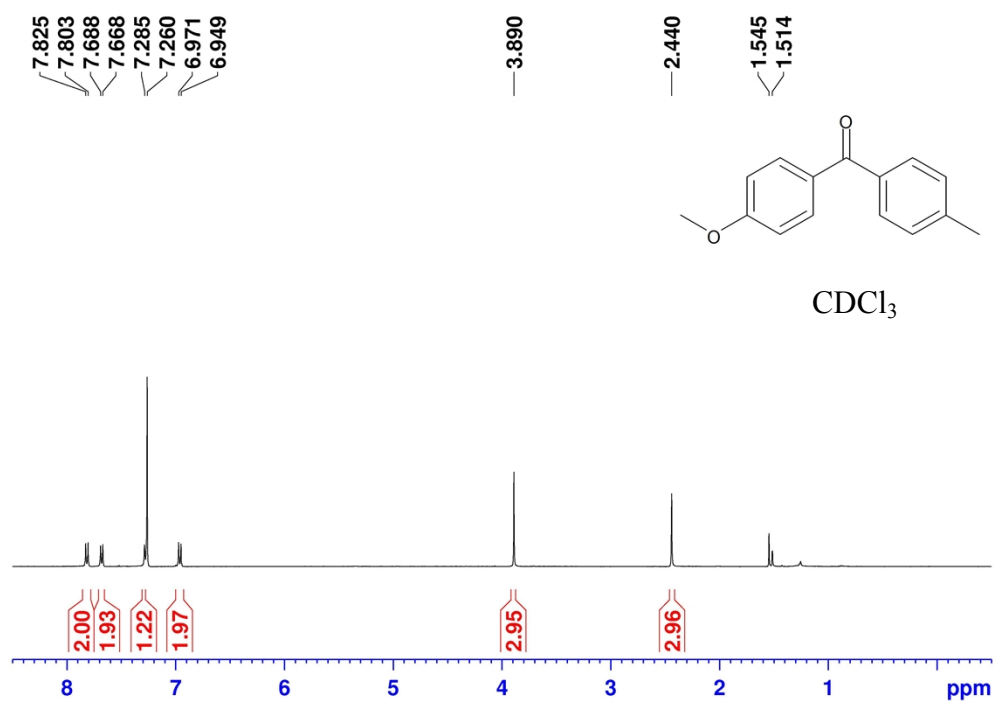
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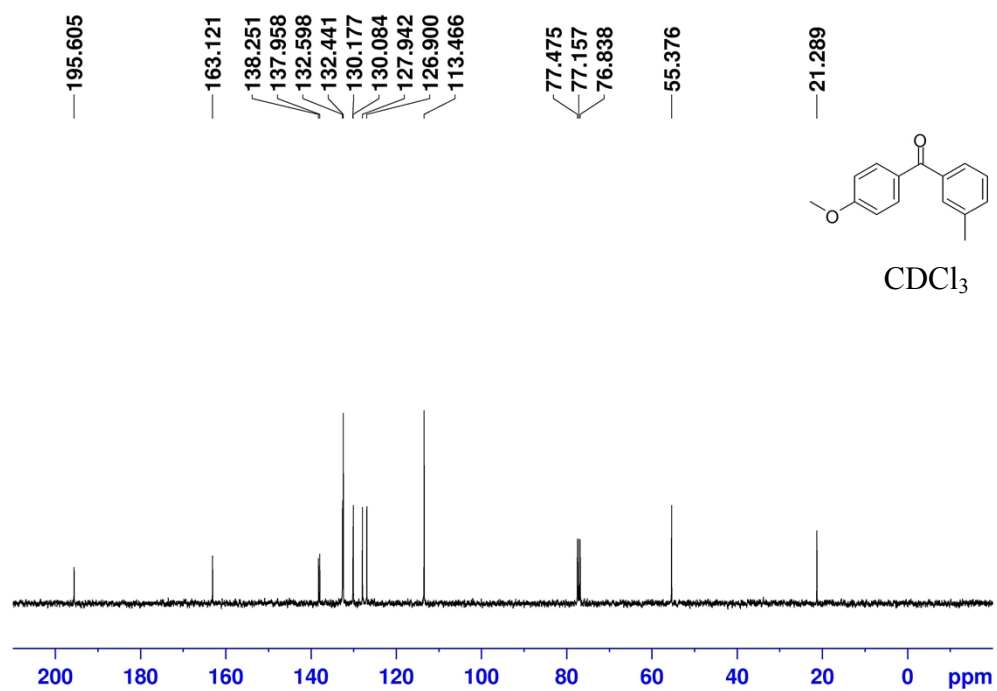
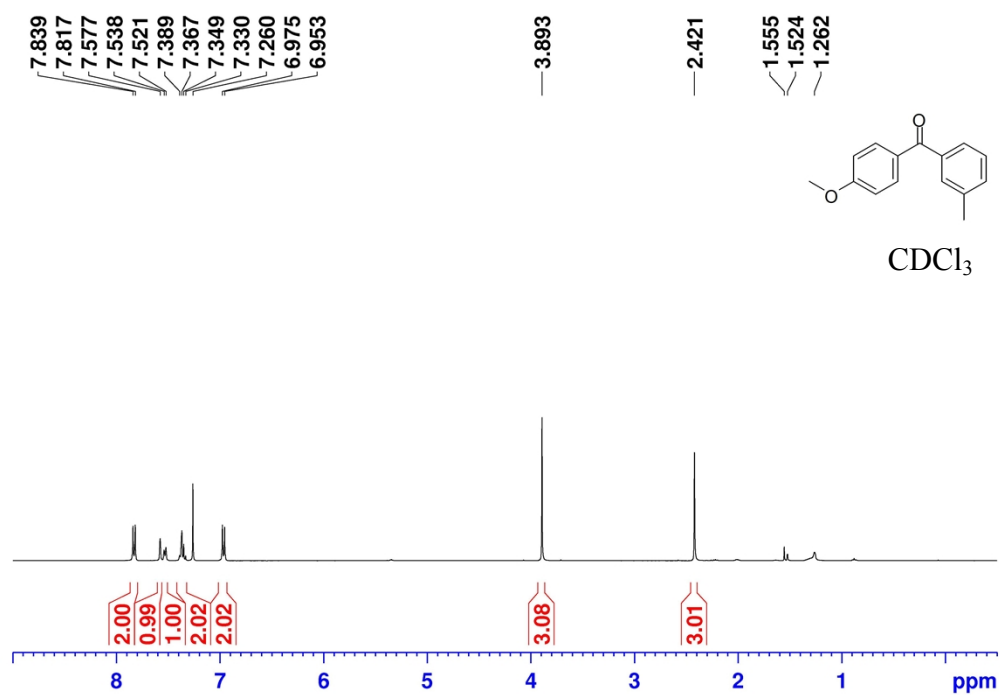
(3-Methoxyphenyl)(4-methoxyphenyl)methanone (Table 2, entry 10)



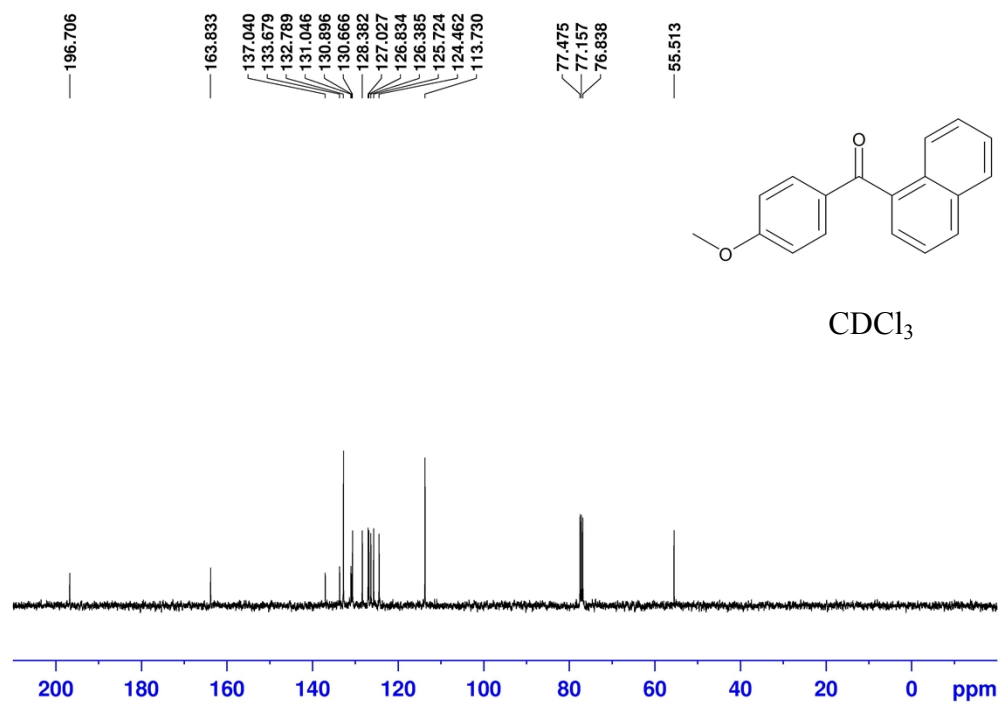
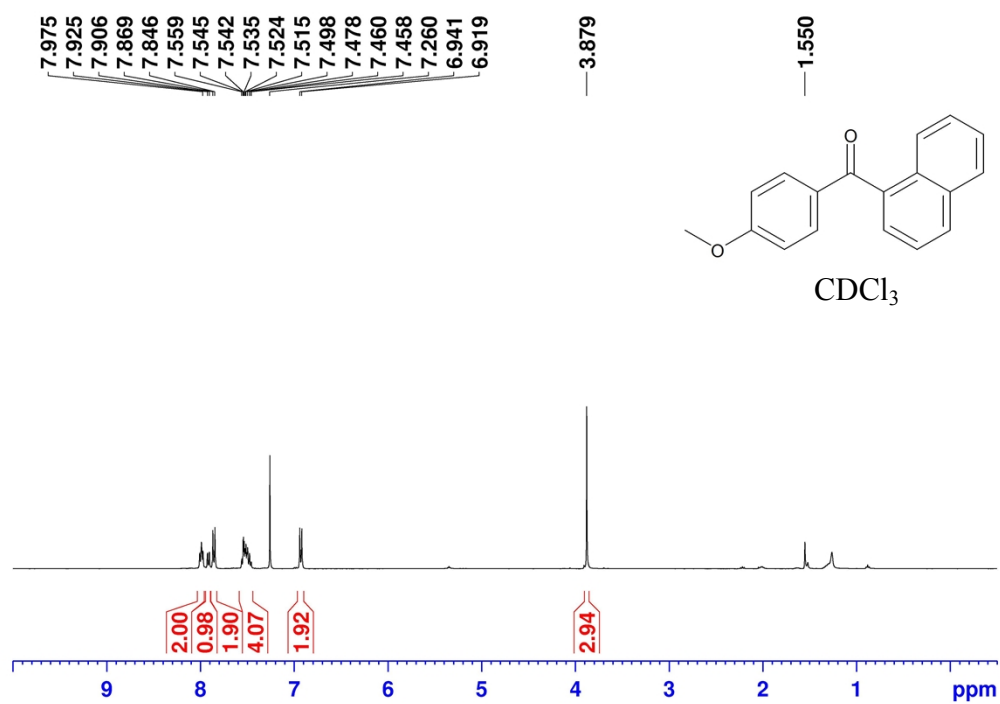
(4-Methoxyphenyl)(*p*-tolyl)methanone (Table 2, entry 11)



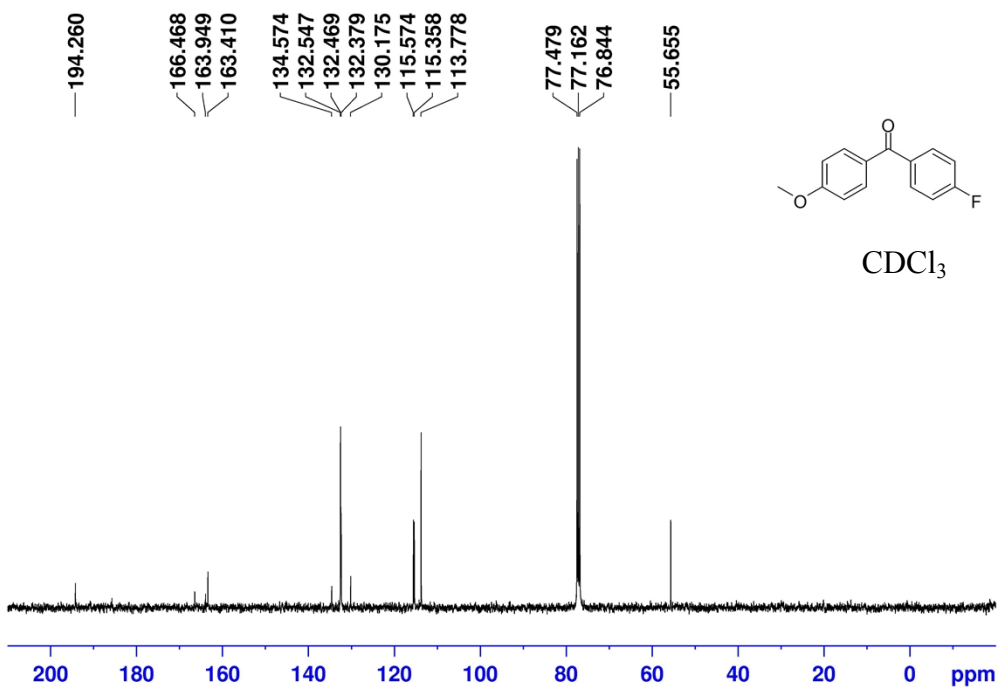
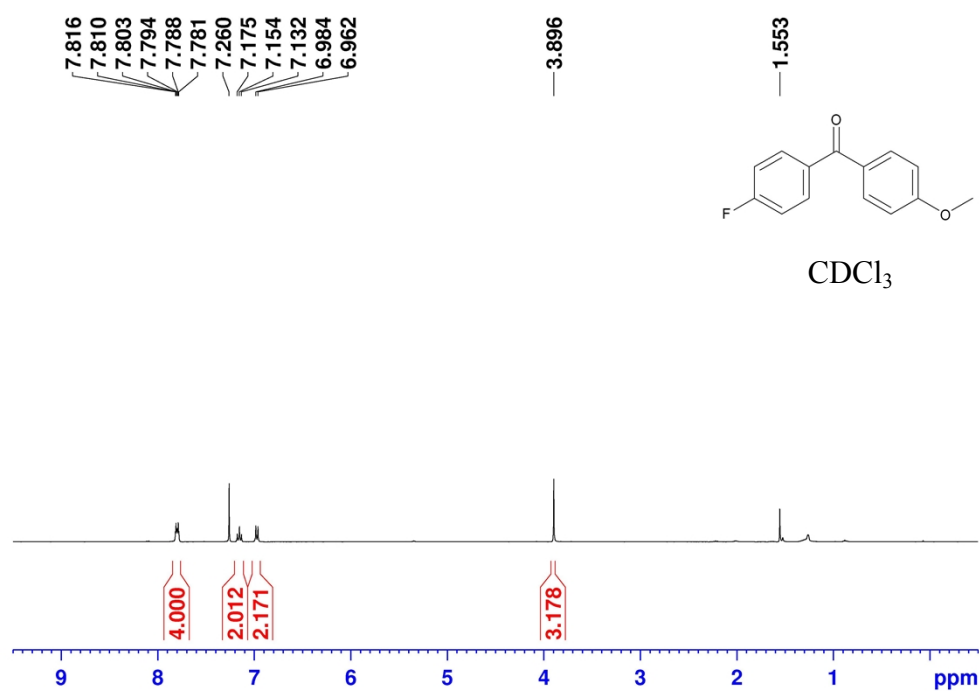
(4-Methoxyphenyl)(*m*-tolyl)methanone (Table 2, entry 12)



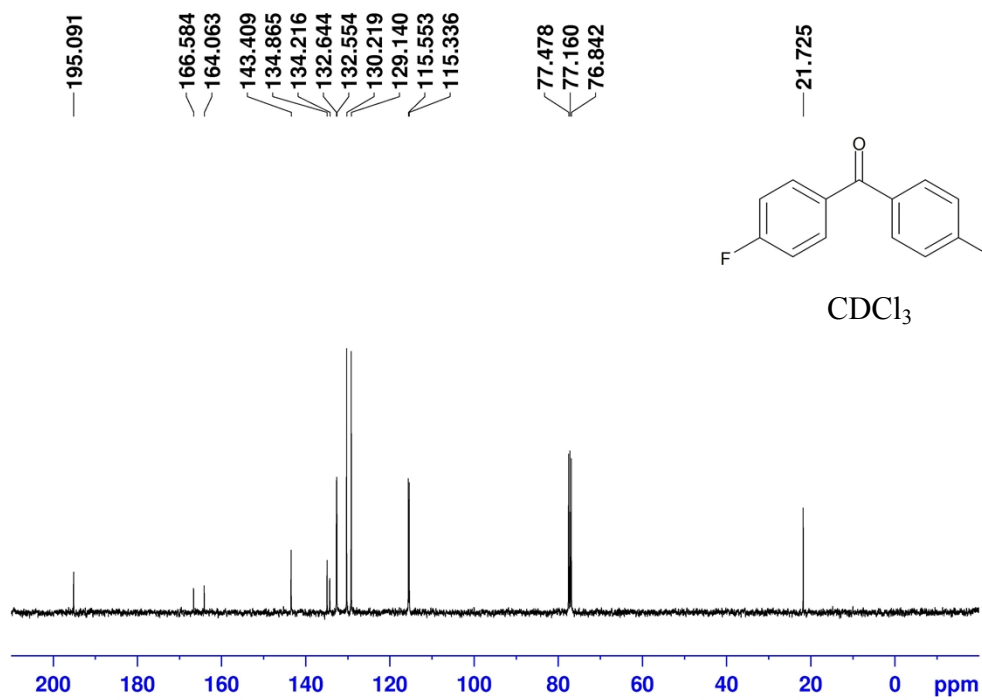
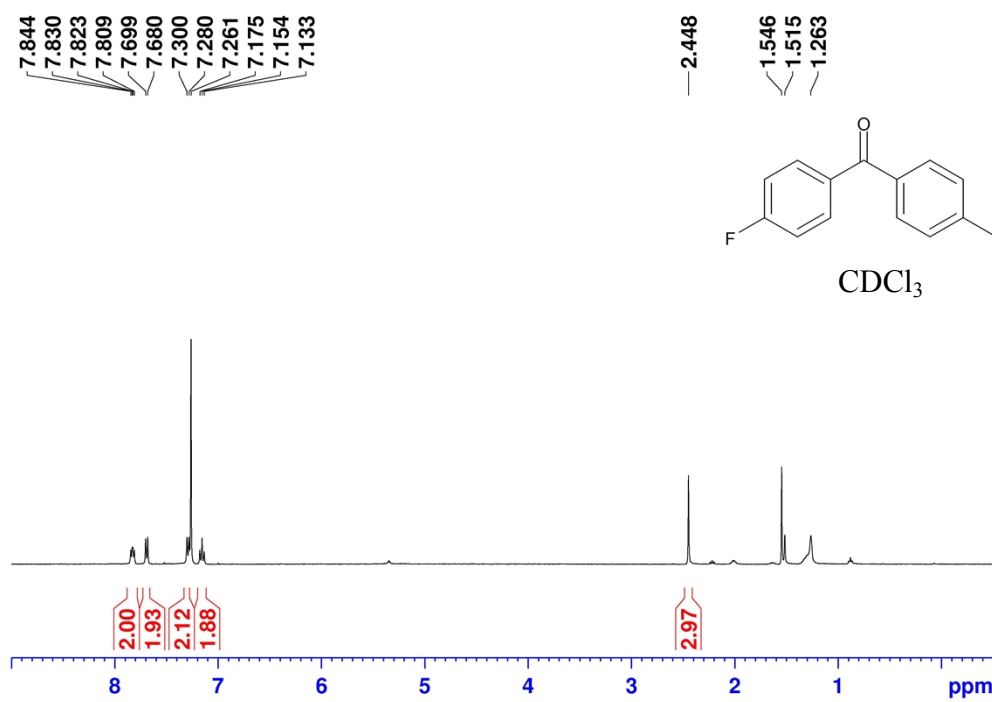
(4-Methoxyphenyl)(1-naphthyl)methanone (Table 2, entry 14)



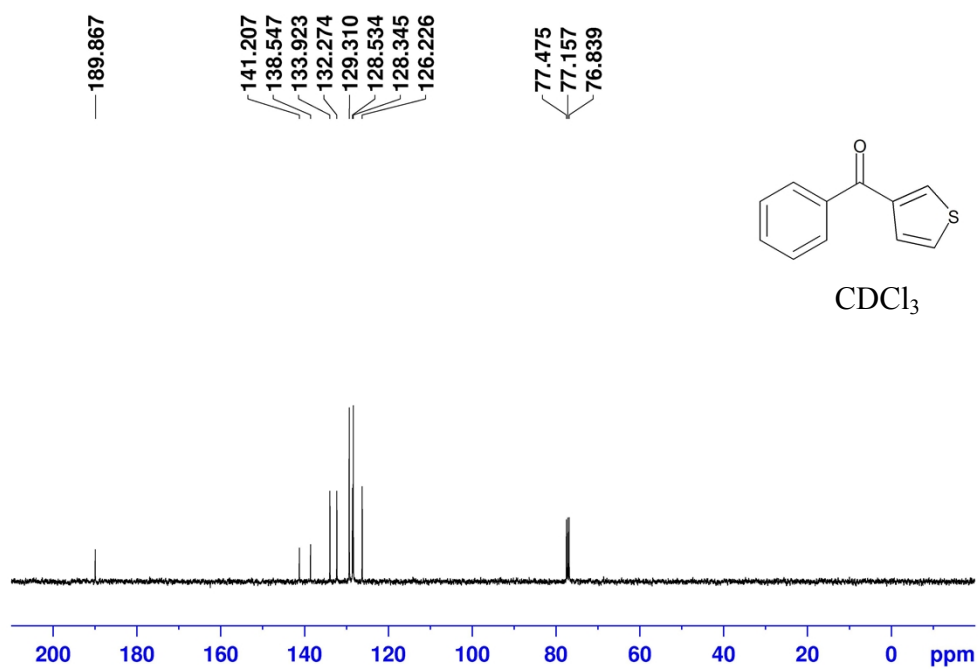
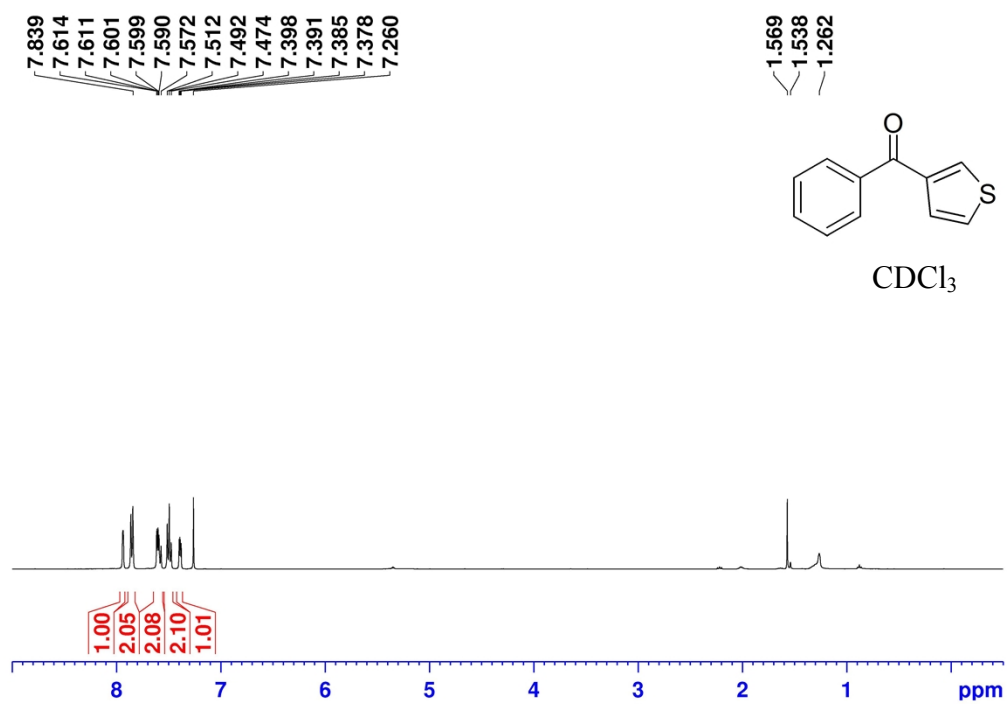
(4-Fluorophenyl)(4-methoxyphenyl)methanone (Table 2, entries 16 and 17)



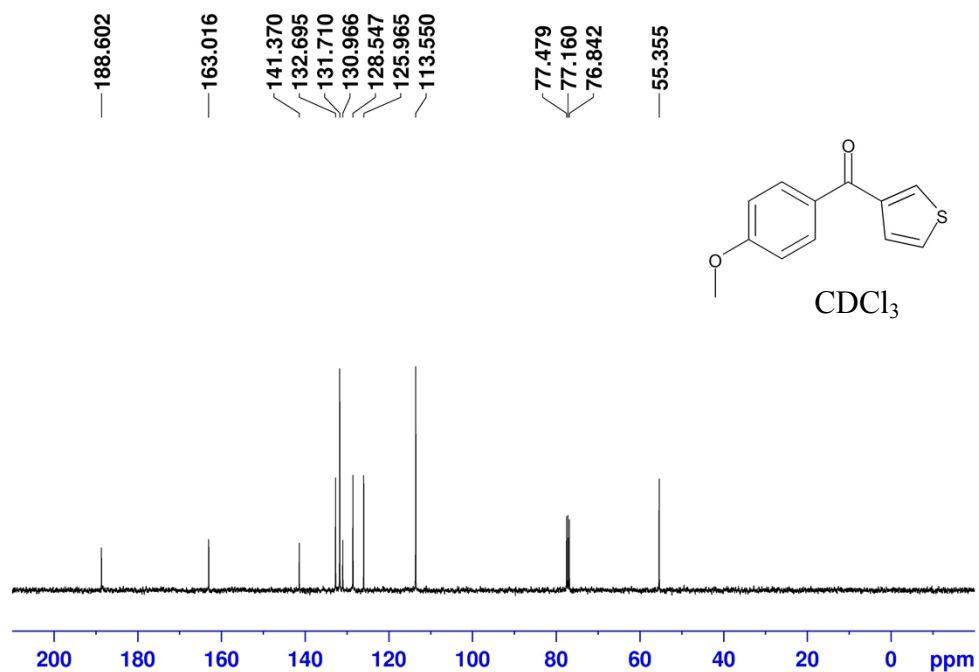
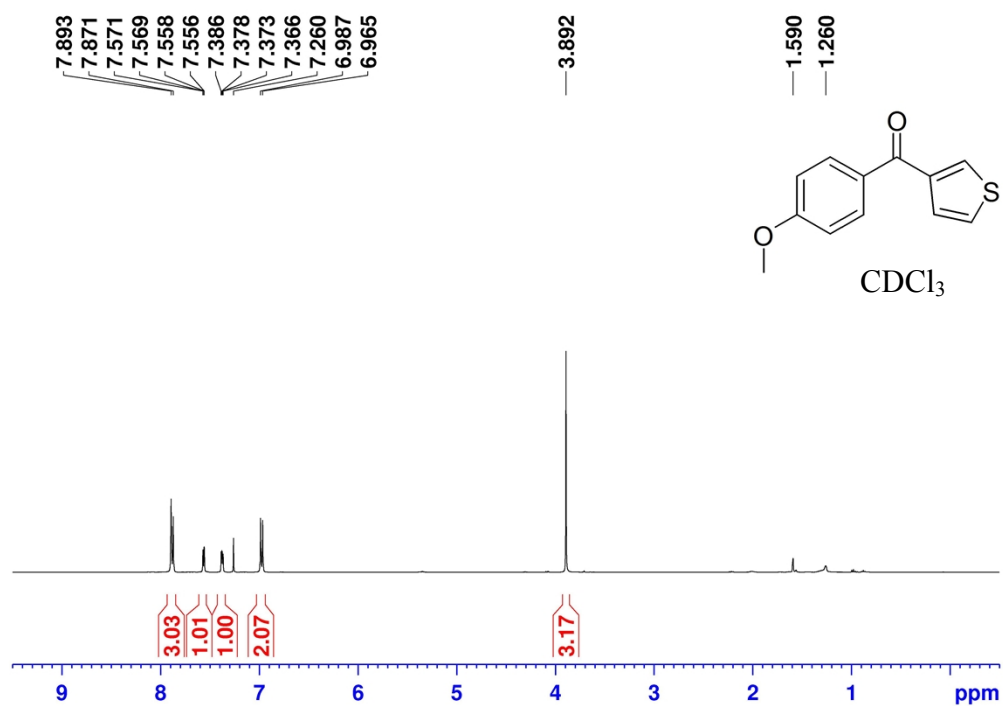
(4-Fluorophenyl)(*p*-tolyl)methanone (Table 2, entry 18)



Phenyl(thiophen-3-yl)methanone (Table 2, entry 23)



(4-Methoxyphenyl)(thiophen-3-yl)methanone (Table 2, entry 24)



(4-Fluorophenyl)(thiophen-3-yl)methanone (Table 2, entry 25)

